A CHEMICAL AND ECOTOXICOLOGICAL ASSESSMENT OF MARINE TAILINGS DISPOSAL AT TWO FORMER COPPER MINE SITES IN NEWFOUNDLAND

G. Veinott, T. Hynes, M.R. Anderson, J. Payne, P. Sylvester, J. Kwong, M. Blanchette, N. Dave, D. Gani, D. Hamoutene, J. Chaulk, and J. Meade

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by

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TABLE OF CONTENTS

List of Figures v

List of Tables vi

Abstract vii

1. Introduction 1
   1.1 Metal Toxicology 1

2. Site Description 3

3. Project Elements and Objectives 4
   3.1 Chemical Assessment 5
   3.2 Impact Zone Delineation 6
   3.3 Ecotoxicological Assessment 6

4. Methods 7
   4.1 Chemical Assessment 7
      4.1.1 Lysimeter testing 7
      4.1.2 Investigation of galvanic interaction 10
      4.1.3 Batch leaching and sequential extraction analysis 11
   4.2 Impact Zone Delineation 12
      4.2.1 Hydroacoustic survey 12
      4.2.2 Trace elements in biota 12
      4.2.3 Sediment collection and analysis 13
   4.3 Ecotoxicology 14
      4.3.1 Acute toxicity tests 14
      4.3.2 Bivalve histopathology 14
      4.3.3 Bivalve immunology 15
      4.3.4 Oxidative damage 16
      4.3.5 Neuroendocrine effects 17
      4.3.6 Short term toxicity tests 17
      4.3.7 Avoidance behaviour 18
      4.3.8 Benthic community structure 19

5 Results 20
   5.1 Chemical Assessment 20
      5.1.1 Site assessments and observations 20
      5.1.2 18 hour leach test 20
      5.1.3 Sequential extraction analyses 21
      5.1.4 Galvanic interactions 24
      5.1.5 Lysimeter studies 25
   5.2 Impact Zone Delineation 31

5.2.1 Hydroacoustic survey 31
5.2.2 Composition of on-land and marine tailings 32
5.2.3 Metal concentrations in the near-shore biota 35
5.3 Ecotoxicology 37
5.3.1 Acute toxicity 37
5.3.2 Bivalve histopathology 37
5.3.3 Bivalve immune response 38
5.3.4 Oxidative damage 38
5.3.5 Short term toxicity 39
5.3.6 Neuroendocrine effects 40
5.3.7 Habitat avoidance 40
5.3.8 Benthic community structure 41

6 Discussion 42
6.1 Chemical assessment 42
6.2 Metal distribution in biota and sediment 43
6.3 Ecotoxicology 44

7 Conclusions 45

8 Acknowledgements 46

9 References 47

LIST OF FIGURES

Figure 2.1 Map of the island of Newfoundland 3
Figure 2.2 Schematic of Little Bay mine and surrounding area 4
Figure 2.3 Schematic of Tilt cove mine and surrounding area 5
Figure 4.1 Experimental arrangement and schematics of the aquarium type diffusion lysimeter 7
Figure 4.2. Experimental set-up for habitat avoidance tests 18
Figure 5.1 Partition pattern for Cu in Tilt Cove tailings 23
Figure 5.2 Partition pattern for Cu in Little Bay tailings 23
Figure 5.3 Little Bay tailings under fresh water cover 27
Figure 5.4 Little Bay tailings under saline water cover 28
Figure 5.5 Tilt Cove tailings under fresh water cover 29
Figure 5.6 Tilt Cove tailings under saline water cover 30
Figure 5.7 Profile across east basin of Little Bay 32
Figure 5.8 Profile across Tilt Cove 32
Figure 5.9 Copper concentrations in sediment at Tilt Cove 34
Figure 5.10 Copper concentrations in sediment at Little Bay 34
Figure 5.11 Lead isotopic composition of on-land and marine tailings 35
Figure 5.12 Metals in mussels. Plot of scores on the first two principle components 36
Figure 5.13 Metals in *Fucus* spp. Plot of scores on the first two principle components 36
Figure 5.14 Metals in *Fucus* spp. and mussels. Plot of scores on the first two principle components 37
Figure 5.15 TBARS concentrations in clams exposed to tailings leachate 39
Figure 5.16 TBARS concentrations in clams sampled at Little Bay and the control site 39
Figure 5.17 Juveline trout exposed to tailings lechate and a control 40
Figure 5.18 Proportion of time juvenile winter flounder spent on either tailings or control sediment 41

LIST OF TABLES

Table 4.1 Leachate exposure parameters 15
Table 4.2 Analysis of dry sediment 19
Table 5.1 Results of the 18-hr leach test using fresh and saline water as a test medium 21
Table 5.2 Concentrations of metals measured in fresh and saline mediums at the end of the galvanic interaction experiment 24
Table 5.3 Bulk chemical compositions of the Little Bay and Tilt Cove tailings .. 25
Table 5.4 Mineralogical compositions of the Little Bay and Tilt Cove tailings ... 26
Table 5.5 Major element composition of Tilt Cove and Little Bay tailings 33
Table 5.6 Trace element composition of Tilt Cove and Little Bay tailings 33
Table 5.7 Serum protein concentrations in mussels exposed to tailings leachate 38
Table 5.8 Polychaete growth rates 40
Table 5.9 Analysis of the benthic community at Little Bay 41

ABSTRACT

Veinott, G., T. Hynes, R. Anderson, J. Payne, P. Sylvester, J. Kwong, M. Blanchette, N. Davé, D. Gani, D. Hamoutene, J. Chaulk, and J. Meade. 2002. A chemical and ecotoxicological assessment of the impact of marine tailings disposal at two former copper mine sites in Newfoundland. Can. Tech. Rep. Fish. Aquat. Sci. 2435: x + 58 p.

The objective of this project was to assess the long-term environmental and ecotoxicological consequences of submarine tailings disposal at two former copper mines in Newfoundland. The project consisted of three elements: 1. Chemical Assessment; 2. Impact Zone Delineation; and 3. Ecotoxicological Assessment.

The results of the chemical assessment demonstrated that Tilt Cove tailings were more reactive than Little Bay tailings, and increased amounts of Al, Co, Cu, Mn, Pb, Si and Zn were released from the former when disposed under a saline and oxic water environment. In the laboratory testing, the concentrations of Cu, Ni, Pb and Zn in the shallow, surface water cover over Tilt Cove tailings under saline water conditions were as high as 13.5, 0.3, 1.0 and 25 mg/L, respectively. The release rates of these metals after development of acidic conditions at the tailings surface were higher by ~50% or more in the saline water cover than those in the fresh water cover. The laboratory tests, however, were conducted under shallow water cover, no flow and room temperature conditions, which were conducive to an enhanced surface reactivity. Therefore, any release of metals in a true tailings disposal scenario would be different and possibly of lower concentrations and at a slower rate than was observed under laboratory controlled conditions.

Nevertheless, concentrations of various elements were elevated in the bivalves and seaweed at both tailings disposal sites. Maximum concentrations of Cu and Mn in bivalves (30 and 5 ppm respectively) were 4x higher at the study sites than at the control site and concentrations of Co (4 ppm) were 9x higher. In the seaweed samples the maximum Cu concentration (120 ppm) was 40x higher than at the control site, while Co concentrations (10 ppm) were 10x higher. At Little Bay, owing to the topography, the tailings are believed to be confined to Little Bay Arm. Copper in the biota decreased with distance from the tailings disposal site with no evidence of elevated Cu concentrations in sediment or biota outside Little Bay Arm. At Tilt Cove, sediment data and analyses of the biota suggest that the tailings have moved outside the defined study area. This is likely due to the prevailing currents in the open ocean environment and suggests that at a 50 m disposal depth, metals from the tailings can still be accumulated by the near shore biota.

There were no overt toxic effects of exposure to the tailings on the biota living at the two sites. Bivalves and seaweed were abundant and in apparent good health. However, evidence was found of long term chronic effects. Most notably were immune system responses by bivalves. Such responses are interpreted as indicating a detoxifying reaction by the organism, suggesting that the tailings are

perceived by the organism as harmful. It was not determined if the immune system response arose from a chemical effect (i.e., presence of toxic metals) or a physical impact (i.e., tailings particle size and sharpness). As well, juvenile trout exposed to tailings leachate exhibited an endocrine system reaction which turned their skin dark. This response has been demonstrated with organic contaminants, but this is the first time it has been observed with exposure to mine tailings.

RÉSUMÉ

L'objectif du projet était d'évaluer les conséquences environnementales et écotoxicologiques à long terme de l'élimination des résidus sous-marins de deux anciennes mines de cuivre à Terre-Neuve. Le projet se divisait en trois volets : 1. évaluation chimique; 2. délimitation de la zone d'impact; 3. évaluation écotoxicologique.

Les résultats de l'évaluation chimique indiquent que les résidus miniers de Tilt Cove étaient plus réactifs que ceux de Little Bay, et que ces derniers produisaient de plus grandes quantités de Al, Co, Cu, Mn, Pb, Si et Zn lorsqu'ils étaient éliminés dans de l'eau salée et oxique. En conditions d'eau salée, les analyses de laboratoire révèlent que les concentrations de Cu, Ni, Pb et Zn sont respectivement de 13,5, 0,3, 1,0 et 25 mg/L dans la couverture aqueuse peu profonde recouvrant les résidus de Tilt Cove. Après la production de conditions acides à la surface des résidus, les taux de rejet de ces métaux dans la couverture aqueuse salée dépassent d'au moins 50 % ceux de la couverture d'eau douce. Cependant, les analyses de laboratoire ont été effectuées avec une couverture aqueuse peu profonde, sans écoulement et à la température ambiante; ces conditions étaient propices à l'augmentation de la réactivité en surface. Par conséquent, le rejet de métaux en situation réelle d'élimination de résidus miniers serait différent de celui mesuré en laboratoire : les concentrations seraient probablement plus faibles et leur rejet se ferait moins rapidement qu'en laboratoire.

Néanmoins, les concentrations de divers éléments étaient élevées dans les bivalves et le varech aux deux lieux d'élimination de résidus. Les concentrations maximales de Cu et de Mn (respectivement de 30 et 5 ppm) étaient 4 fois plus grandes dans les bivalves des sites d'étude qu'au site témoin, et les concentrations de Co (4 ppm) étaient 9 fois plus grandes. Dans les échantillons de varech des sites d'étude, la concentration maximale de Cu (120 ppm) était 40 fois plus élevée qu'au site témoin, tandis que celle du Co (10 ppm) était 10 fois plus élevée. En raison de la topographie des lieux, on pense que les résidus sont confinés au bras de Little Bay. Les concentrations de cuivre dans le biote diminuent en fonction de l'éloignement du site d'élimination des résidus et rien n'indique que les concentrations de Cu dans les sédiments ou le biote à l'extérieur du bras de Little Bay sont élevées. À Tilt Cove, les données relatives aux sédiments et les analyses du biote laissent croire que les résidus se sont déplacés à l'extérieur de la zone d'étude. Cette situation a probablement été causée par les courants dominants en

haute mer, qui peuvent faire en sorte que des métaux provenant de résidus éliminés à une profondeur de 50 m peuvent s'accumuler dans le biote du littoral.

L'exposition aux résidus n'a entraîné aucun effet toxique manifeste sur les organismes vivants des deux sites, où se trouvaient de grandes quantités de bivalves et de varech apparemment en bonne santé. Cependant, on a observé des effets chroniques à long terme : le système immunitaire des bivalves a été particulièrement touché. Cela indiquerait que l'organisme a une réaction de détoxification et qu'il perçoit les résidus comme nuisibles. L'étude ne précise pas si la réaction du système immunitaire était causée par un effet chimique (c.-à-d. la présence de métaux toxiques) ou un impact physique (à savoir la taille et l'abrasivité des particules de résidus). Par ailleurs, le système endocrinien d'alevins de truite exposés aux lixiviats des résidus a réagi en fonçant la couleur de la peau. Une telle réaction avait déjà été notée en ce qui a trait aux contaminants organiques, mais c'est la première fois qu'elle est liée à l'exposition aux résidus de mine.

PREFACE

This technical report is a synopsis of the final report of the Toxic Substance Research Initiative (TSRI) project #130: *A chemical and ecotoxicological assessment of marine tailings disposal*. The TSRI was administered by Health Canada who provided the bulk of the funding for this project. The collaborating partners were Natural Resources Canada, Memorial University, and Fisheries and Oceans Canada.

1 INTRODUCTION

The processing of ore at mine sites throughout the world generates large amounts of solid wastes (tailings), which contain residual concentrations of all metals originally present in the ore. The tailings frequently contain substantial concentrations of unoxidized sulfides. The subsequent oxidation of sulfides can form acid, mobilize the metals present, and release them into the environment.

In Canada, tailings were historically discharged directly into the environment (including the ocean), but over the past several decades the practice has been to impound tailings behind retaining dams. During the last decade it has been shown that storage of tailings under water has been highly successful in preventing further oxidation, and where site conditions permit, this has become the preferred disposal option. The chemistry and reaction kinetics of tailings stored under fresh water are now well known, but questions of long-term ecotoxicological effects of metal seepages and releases are still poorly understood. In British Columbia and Atlantic Canada, submarine tailings disposal (STD) may be the safest option in some cases, however, since the science of leaching under saline versus fresh water, the pH buffering impact of sea water, and the biological impacts in the marine environment are so poorly known, that there are no operating permits currently in effect. For the majority of historical tailings depositions into the ocean, there is little knowledge of the impacts on water, sediment, or biota, but many deposits are located in areas where impacts could be expected if metals were mobilized. There is a great need to understand the impacts of marine tailings disposal, evaluate historical deposition, and generate the sound science required for regulatory control of toxic metals in mining wastes.

1.1 METAL TOXICOLOGY

Exposure of humans and other organisms to trace metals is increasing both in terms of concentrations and different metal species. Mechanisms have evolved over time which permit organisms to utilize essential metals as integral parts of their structure and function. However, non-essential toxic metals may compete with essential metals having similar chemical properties. When concentrations of competing toxic metals are low, essential metals can out-compete them for binding sites, but as concentrations of non-essential metals rise, they begin to interfere with the normal functions of essential metals. Such interference can result in a variety of toxic outcomes (Seiler et al. 1988; Chang et al. 1996). In the meantime, overload of such essential elements as copper, iron, selenium, nickel, zinc, cobalt, and molybdenum can also produce severe toxicity.

Metals have been linked to overt health effects in humans (e.g., Seiler et al. 1988; Chang et al. 1996). For example, aluminum, mercury and lead have been associated with neural dysfunction; nickel, lead, chromium and cadmium with cancer; and cadmium and arsenic with organ debilitation. A wide variety of mutagenic, teratogenic, reproductive, neurological, immunological and general organ effects have also been observed in rodent and other experimental models

with heavy metals. This includes effects of such essential metals as copper. For instance, effects noted in sheep exposed to relatively high concentrations of copper included liver damage, impaired reproduction and reduced resistance to disease (Eisler 1997). Likewise, a variety of biochemical, physiological and histopathological effects have been documented in fish (and other organisms) on exposure to trace elements such as selenium and arsenic, and metals such as lead, cadmium, copper and mercury (Sorensen 1991).

With respect to humans, wildlife or other organisms, little is known about mechanisms of toxicity or the role played by elevated levels of metals in cellular toxicity and thus any overall enhancement of organism morbidity and mortality. To date most of the emphasis on the toxicity of metals to aquatic organisms has been on the effects of free metal ions on ionic and osmotic functions (e.g., Kramer et al. 1997; Wood et al. 1997). However, given the various types of pathologies associated with heavy metals, it is realized that other mechanisms of toxicity may be more important for most aspects of chronic toxicity. For instance, the potential of various metals to produce oxidative damage to DNA and other macromolecules is a topic of considerable biomedical interest (e.g., Davies 1991). It has also been recently demonstrated that certain metals may play such diverse roles as directly inhibiting DNA repair processes or provoking transmembrane signals and oncogene induction (e.g., Smith et al. 1994). Likewise, the direct or indirect effects that metals have on such physiological processes as reproductive hormone balance or immunological competence would also be important in relation to chronic toxicity (Gerhard et al. 1998).

Metals from mining activities are released into the environment either as metal ions which form complexes with naturally occurring complexing agents or as various types of specific mineral-related particulates. The more acutely toxic effects of metals are ion-related and such toxicity can be modulated by the presence of similar ions or the formation of various inorganic and organic complexes (e.g., Fernando 1995; Wood et al. 1997; Chapman et al. 1998). Regulatory practices have traditionally focused on ion toxicity and the well known fact that various ligands can reduce the acute toxic effects of metals. However, it is now realized that the myriad of metal complexes which may form in the environment and become bioavailable to different organisms through various routes could play an important role in chronic toxicity. Also, stable mineral-related microparticulates which are essentially non-toxic in terms of acute toxicity can be sequestered by cells and effect various pathologies (Costa et al. 1994). Marine flat fish which may ingest considerable levels of metal-laden material from interstitial water in sediments and, bivalves which may filter out metal-laden particulates from the water column are both prototype examples of chronic exposures of considerable toxicological interest and for which essentially no information is available for assessing risk.

In addition to concerns for human and wildlife health stemming from both elevated levels of metals and different metal species entering the environment, there is rising concern over whether the concentrations of metals entering the aquatic environment pose longer-term ecotoxicological risks. The primary

objective of this project, therefore, was to assess the long-term environmental and ecotoxicological consequences of marine tailings disposal.

2 SITE DESCRIPTION

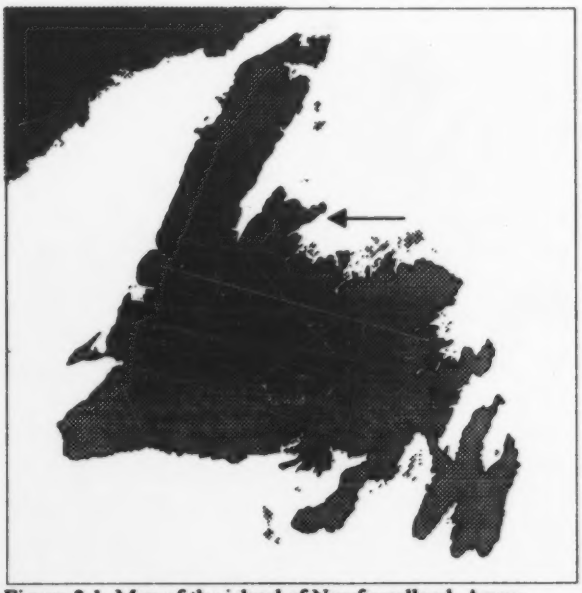

Figure 2.1. Map of the island of Newfoundland. Arrow indicates approximate location of the study sites

The two sites selected for this study are located on the north east coast of the island of Newfoundland on the Notre Dame Peninsula (Fig. 2.1). They are free of confounding effects from other major sources of industrial or urban contamination and provide ideal conditions for evaluating the biological impact of complex mixtures of metals. Both sites are former copper mines with large quantities of tailings present in the marine environment. The production history and geological and physical attributes of these sites have been compiled from available documentation (Dimmell 1999), a brief overview of which is presented below.

At the first site, Little Bay (Fig. 2.2), the mine was first worked from 1878 to 1893 and again in 1918. The mine was reactivated in 1961 and operated until 1969 with production totalling ~2,572,000 tonnes of 0.8-2% copper. A total of ~1.8 M tonnes of tailings were generated during this phase of mining and placed in an impoundment area formed by damming off a shallow mixed marine/freshwater bay (Fig.2.2 'Tailings'). The tailings dam breached around 1988 and an estimated 30-50% of the tailings have subsequently been washed out into Little Bay Arm and form a tailings delta below the dam (Fig. 2.2).

At the second site Tilt Cove (Fig. 2.3), mineralization was discovered in 1857 and the mine was first worked between 1864 and 1918. No tailings were produced in this early phase of mining, however at least one shipment of ore is reported to have floundered off Tilt Cove. The property was reactivated in 1957 and operated until 1967 at 2,000 tons/day, producing ~468,000 short tons of copper concentrate from approximately 7.4M tonnes of ore grading approximately 1.5% copper. In this production phase, tailings were slurried by pipeline into 50 m of water in a high energy environment just to the south-west of the harbour (Fig. 2.3). The total tonnage of tailings deposited into the marine environment is

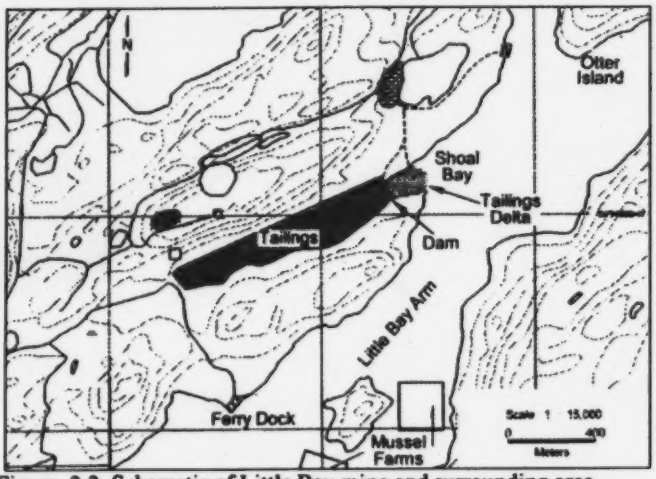

Figure. 2.2. Schematic of Little Bay mine and surrounding area.

unknown but is at least 5-6 million tons, with an estimated particle size of 95% less than 200 mesh and 70-80% less than 325 mesh.

3 PROJECT ELEMENTS AND OBJECTIVES

The principal objective of the project was to assess the long-term environmental consequences of submarine tailings disposal. Subaerial (i.e. open air) disposal of reactive sulfidic tailings, like those produced at the study sites, frequently lead to the generation of acid mine drainage (AMD). AMD, once generated, is difficult and expensive to control and may cause severe ecological impacts (Axtmann and Luoma 1991; Erickson and Deniseger 1987). AMD prevention is the preferred strategy to minimize potential environmental impacts of mining projects. Recent research has shown that subaqueous disposal of mine waste is an efficient means to suppress sulfide oxidation and hence the generation of AMD (MEND 1990a, 1990b, 1992; Pederson and Losher 1988). The feasibility of installing a fresh water cover on mine waste frequently depends on the availability of non-productive natural lakes or involves construction of retaining dams for man-made facilities. In coastal regions where deep, restricted submarine basins occur, mine wastes may be disposed below the light-penetration zone with little ecological impact (Poling and Ellis 1993; Ellis et al. 1995).

To substantiate the applicability of mine waste disposal under either a fresh or saline water cover, a detailed assessment of metal leachability of the mine waste and its potential impact on the local biota is indispensable. The critical information required includes: the nature of the metal and its rate of release in bioavailable form as a result of subaqueous disposal; how metals are taken up by biota; and the impact/consequence of metal uptake. To address the above issues and meet the primary objective, the project was divided into three elements: chemical assessment, impact zone delineation, and ecotoxicological assessment.

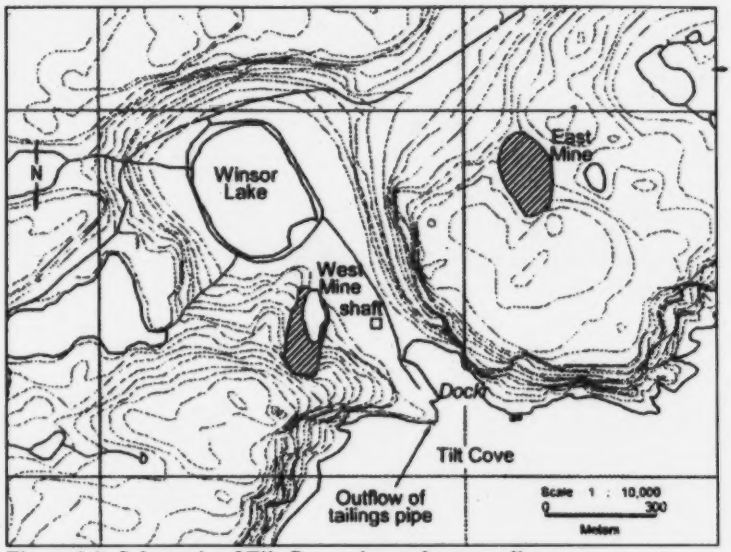

Figure 2.3. Schematic of Tilt Cove mine and surrounding area.

3.1 CHEMICAL ASSESSMENT

The major objectives of the Chemical Assessment project element were to: assess the actual versus potential oxidation and availability of metals at the study sites; determine the potential oxidation and availability of metals in mine wastes under saline vs. fresh water cover; and, determine ranges of contaminant levels in overlying and pore water over time to which the biota may be exposed. The research activities included:

- A reconnaissance survey to examine local geology and assess evidence of chemical weathering;
- Sampling fresh and saline waters as well as marine tailings/sediments and tailings disposed on land for detailed geochemical characterization;
- Batch leach testing to determine potential instantaneous metal releases;
- Sequential extraction analysis on a select suite of samples to decipher metal partitioning;
- Galvanic interaction studies to assess metal leaching under fresh/saline water cover; and
- Long-term lysimeter testing for trends in metal influx to or efflux from tailings disposed under water.

3.2 IMPACT ZONE DELINEATION

Once tailings enter the marine environment, the associated metals will be dispersed in a number of ways. Tailings will settle and slump depending on physical contours of the disposal site and the hydrodynamic regime of the water column. Wave action and ice scour will tend to resuspend the finer particles of the tailings and disperse them to deeper settling areas. Sediment-bound metals, associated primarily with the fines will be transported in this manner. Sediment diagenesis, diffusion and pore water movement will release metals into solution in the water column. Most will eventually flocculate with organic matter and tend to settle out in deeper sites with low currents. As a result, biota can be exposed to metals in ionic form or may come in contact with metals bound in organic floc or fine sediments through ingestion or burrowing. The objectives of this project element were to determine the movement and fate of metals from the tailings and measure the accumulation in nearby biota. The major tasks included the following:

- Hydroacoustic Survey to delineate physical contours of tailings;
- Delineation of tailings dispersal using Pb isotope ratios and trace element ratio fingerprinting; and
- Sampling and subsequent chemical analysis to assess metal accumulation in biota.

3.3 ECOTOXICOLOGICAL ASSESSMENT

The overall aim of the ecotoxicology project element was to define and delineate risks associated with chronic as well as acute toxicity. The focus was on chronic toxicity because metal complexes and particulates have little acute toxicity potential. Major tasks included:

- Survival tests on juvenile flounder, trout larvae, capelin larvae, and mixed plankton samples;
- Bivalve histopathology;
- Bivalve immune response tests;
- Testing for evidence of oxidative damage to cell membranes and DNA;
- Short-term toxicity tests (Microtox, amphipod survival, polycheate survival);
- Neuroendocrine effects tests;
- Habitat avoidance tests; and
- Examination of benthic community structure.

4 METHODS

4.1 CHEMICAL ASSESSMENT

4.1.1 Lysimeter Testing

4.1.1a Experimental arrangement: The laboratory studies of underwater deposited tailings were conducted in clear aquarium-type diffusion lysimeters. A total of four lysimeters, two each containing tailings from the Little Bay and Tilt Cove sites under fresh and saline water conditions were prepared. Each lysimeter consisted of a clear aquarium-type chamber made from welded polycarbonate sheets, and measured 1.22 m in length, 0.30 m in width and 0.60 m in height with a nominal wall thickness of 9.5 mm. A rigid, 50 mm x 50 mm x 6.3 mm, steel angle frame supported the lysimeter at the sides and bottom for structural integrity. Figure 4.1 shows the schematic of the aquarium-type lysimeter

Each lysimeter contained at the bottom, a filter and support bed, 50 mm in height, consisting of coarse, high-density polyethylene pellets of nominal size (~ 3 mm in diameter) and covered with a 100 μm pore size polypropylene filter

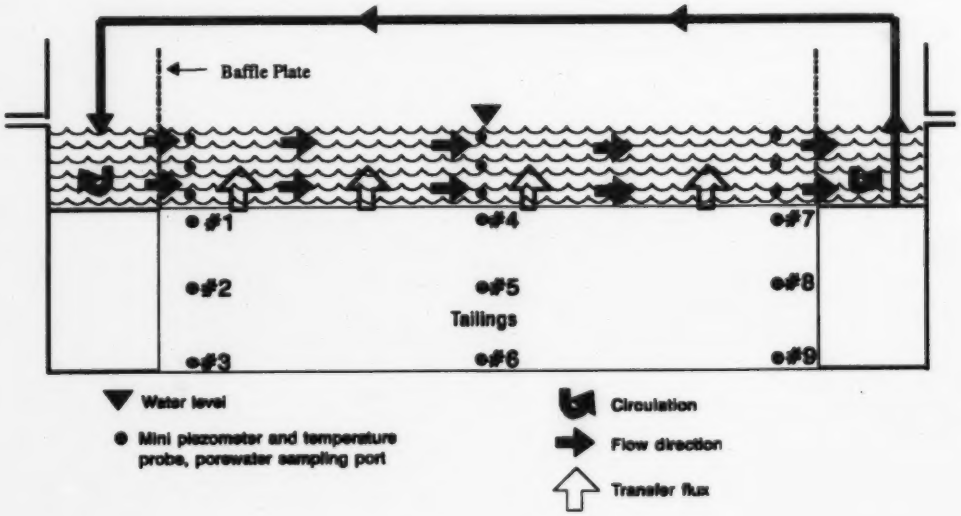

Figure 4.1. Experimental arrangement and schematics of the aquarium-type diffusion lysimeter.

fabric. The test tailings, up to 0.3 m in height, were gradually placed above the filter bed. After displacing trapped air from the bottom, the lysimeters were gradually filled with fresh or saline water to provide a water cover approximately 0.2 m above the tailings. The filter bed space provided a buffer volume for pore water drainage and flow.

The lysimeter also had two side chambers, each approximately 0.15 m in width, with perforated baffle plates in the upper half for mixing of the water column and providing stream-line flow along the tailings – water interface. The water column above the tailings was continuously mixed during the experimental period to prevent stratification, varying concentration gradients and thermal eddy currents in the column. The mixing of the water column provided a single concentration gradient normal to the tailings-water interface. The baffle plates prevented turbulent water flow along the surface of the tailings.

Each lysimeter had a total of six rows of mini piezometers (three per row) for sampling surface and pore waters at different depths. Nine piezometers in three rows each were in the upper water cover and lower tailings sections. The piezometers were installed along three vertical columns, one along the centre and the other two along equally spaced left and right vertical planes. In the upper water-covered section, the sampling piezometer rows were located at three depths, 0.025 m (near surface), 0.100 m (intermediate) and 0.175 m (near bottom) below the surface of the water. In the lower tailings sections the piezometers were located at depths of 0.025 m (near surface), 0.150 m (intermediate) and 0.275 m (near bottom) below the tailings-water interface. The mini-piezometers were rigid, narrow-diameter clear acrylic tubes in the water cover section and flexible clear PVC tubes in the tailings section. The piezometers, approximately 0.1 m in length and 6.3 mm in nominal diameter, were perforated along the lengths and covered with filter fabric socks made from the above mentioned filter material. The piezometers were placed horizontally in the middle, along the width of the lysimeter, and connected to appropriate fittings installed in the front face of the lysimeter for sampling. A similar sampling and drainage port was also installed in the centre at the bottom of the lysimeter.

The lysimeters were loaded with tailings obtained from the Little Bay and Tilt Cove sites. The tailings samples were obtained by hand excavating the unexposed tailings from the surface-deposited tailings pile at the Little Bay site, and tailings buried at a former ballpark at the Tilt Cove site. The fresh water for the cover was obtained from Meach Lake, located approximately 7 km northeast of the city of Ottawa. The saline water was obtained from the sea loading dock at the Tilt Cove site. The tailings were homogenized individually in a cement mixer prior to placement in the lysimeters. In each lysimeter, the tailings were placed at the bottom, up to a height of 0.25 m, and covered with the appropriate water to provide a water column depth of ~0.2 m

While loading, the respective tailings for fresh and saline water cover conditions were mixed with fresh or saline waters to displace trapped air and deposited as a thick paste. The tailings were covered with appropriate water covers up to a height of approximately 0.1 m, and allowed to settle to the desired height and establish pore water equilibrium conditions prior to starting the experiments. During this equilibration period, the tailings pore water was also mixed by pumping from one sampling horizon to another.

During the experimental set-up it was observed that the underwater deposited Tilt Cove tailings were rapidly oxidizing at the surface and within pore space, resulting in increased acidity and low pH surface and pore waters within a

few days. These tailings were found to contain oxidation reaction products from their previous exposure and weathering history at the site. These reaction products were leached when placed under water and contributed to the observed increased acidity and low pH conditions. Oxidation of dissolved Fe^{+2} to Fe^{+3} and its subsequent hydrolysis to precipitate $Fe(OH)_3$ provided additional acidity to the system. These tailings, for both fresh and saline water cover conditions, were removed from the lysimeters and washed individually with laboratory tap water in large high-density polyethylene (HDPE) tanks to remove soluble products. A total of five wash cycles were undertaken, but the tailings continued to produce minor amounts of acidity in the wash water having a pH of ~ 5.0. Further removal of oxidation reaction products was not practical and the respective lysimeters were re-loaded with the washed Tilt Cove tailings.

Once the pore water equilibrium conditions were attained in all lysimeters, the standing surface and pore water samples were obtained for analysis as pre-experimental reference condition. The standing surface water was decanted and the exposed tailings surface in contact with the oxygenated water cover during the equilibration period was removed to start the experiment with a fresh tailings surface at the interface. The lysimeters were re-filled with fresh and saline waters to the desired heights to start the experiments. The tailings were also sampled while loading the lysimeters and after the final surface preparation to obtain two composite solid phase samples for bulk chemical and mineralogical characterizations.

4.1.1b Sampling and measuring procedures: The chemical reactivity of the underwater deposited tailings was evaluated by measuring the surface and pore water quality profiles as a function of time. The lysimeters were designed for measuring mass diffusion or transport fluxes resulting from surface activity and/or pore water diffusion under a no-flow well-mixed water column condition for a single height of water cover above the tailings surface. The height of the water column was approximately 0.2 m for the four lysimeters. A small water pump mixed the water column in the lysimeter by pumping water from the bottom of one baffle chamber and discharging it at the top of the other. The water was discharged above the water surface in the mixing chamber to agitate and aerate the water while mixing inn order to for maintain the oxygen saturation condition. This provided minimal disturbance to the tailings surface, and at the same time, maintained a constant upward concentration gradient between tailings pore water and the upper lying water column. The mass flux of a given pore water constituent was determined by measuring its surface water concentration as a function of time.

The experiments were started after establishing new fresh and saline water covers above the freshly exposed tailings. The mixing pumps were started and the start time was designated as time T= 0 h. At this time, representative surface and pore water samples were obtained. The surface water columns were re-sampled at time intervals of: T = 1 d, 3 d, 7d (1w), 14d (2w), 28 d (4w) and every two weeks there after for an initial period of six months. The composite pore water samples for each horizon were obtained every four weeks. The samples were analyzed for

pH, redox potential (Eh), electrical conductance (Ec), total acidity, total alkalinity and dissolved concentrations of Al, As, Ba, Ca, Cu, Cr, Fe^{+2}, Fe (total), Hg, K, Mg, Mn, Mo, Na, Ni, Pb, S (total), SO_4, Si, Ti and Zn. The study was continued for a period of 1.5 year. Upon completion of the study, the tailings in the lysimeters were sampled at the surface and at depths by extracting core samples for mineralogical and bulk chemical analysis.

For most water samples analyses, the standard methods for the examination of water and wastewater (American Public Health Association, 1992) were followed. The liquid samples were analyzed by Inductively Coupled Plasma Atomic Emission Spectrophotometry (ICP-AES), Atomic Absorption Spectrophotometry (AAS), Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and High Pressure Liquid Ion Chromatography (HPLIC). For trace metals analysis, especially saline water containing high dissolved solids, the metals were first selectively extracted from the aqueous phase into an ion exchange resin followed by elution of the ion exchange resin with a dilute acidic solution, transferring the adsorbed metals into the aqueous eluate solution. The trace metal concentrations in these solutions were measured by ICP-MS.

The solid samples were pulverized and analyzed for their bulk Si, Ti, Al, Fe, Mg, Mn, Ca, Na, K, P, Cu, Zn, Pb, CO3, S (total), and SO4 concentrations by ICP-AES, AAS and LECO techniques. All samples were analyzed by the analytical services group of Mining and Mineral Sciences Laboratories, Ottawa.

The solid phase mineralogy was determined by preparing polished sections and examining the samples by optical microscopy, scanning electron microscopy (SEM), X-ray micro analysis and electron microprobe analysis. The samples were also analyzed using a Rigaku rotating anode X-ray powder diffractometer for mineral identification. X-ray diffractograms were collected under slow conditions with CuKα radiation at 55 kV, 180 mA, a step-scan of 0.04° and a scan rate of 4° per minute in 2θ. Mineral quantities were determined by a combination of linear mixing models of whole rock and mineral compositions and simple subtraction techniques (Paktunc 1998).

4.1.2 Investigation of galvanic interaction

To investigate the potential for preferential metal leaching through galvanic interaction under a shallow water cover, the flow-cell method as described by Lawrence et al. (1997) was adopted. Minor modifications to the documented procedure included the use of a data logger to automatically, rather than manually, monitor the evolution of potential differences at mineral surfaces throughout the experiment and the microbial inoculation was not incorporated. The experiment was conducted at the National Hydrology Centre, Saskatoon, in collaboration with Dr. John Lawrence of the National Water Research Institute. As test material, duplicate polished thin sections were prepared from mineralized grab samples, two each from the Little Bay (LB-1, LB-2) and Tilt Cove (TC-1, TC-2) sites and one from the United Keno Hill Mine (Onek-1) in the Yukon Territory. Samples from the two Newfoundland sites contained mixed sulfide assemblages dominated by pyrite-chalcopyrite or chalcopyrite-pyrrhotite, while

the Yukon sample was characterized by pyrite-sphalerite-galena. One of the duplicate thin sections made from each rock specimen was used in the fresh water flow cells, where the recirculating medium was Meech Lake water, and the other in the saline water flow cells with seawater from Tilt Cove as the recirculating medium.

Each monitoring microelectrode was custom-made by epoxying 0.1 mm diameter, 99.99% Pt. wire into a predrawn micropipette and then grinding it to give a measuring point at 45° on a micropipette beveler with #1500 abrasive paper. The Pt wire was then soldered to a 22 gauge, color-coded polyethylene insulated Cu wire and the connection heat-shrunk wrapped for strength. The flow cells were made of acrylic plastic (Plexiglass). In each cell, there was a well for the thin section slide with a silicone dam to allow an immersion depth of 3 to 4 mm depending on the surface tension of the water used. Each cell was connected to an individual 50 mL reservoir. The side walls of each flow cell were constructed to support a beam with electrode position support tubes attached to it. When the electrodes were positioned on the proper grains, the beam was glued in place. The wires from the electrodes were coiled to provide a downward spring force onto the mineral surface and then wrapped around the flow cell and the ends braided together and labeled for attachment to the multiplexer-data logger system.

Prior to the start of the flow cell experiment, relevant textual features on each the thin section were recorded by photography under a petrographic microscope. The sections were then glued into the flow cells and submerged under 3 to 4 mm of the recirculating water. The microelectrodes were positioned and glued into place. The multiplexers and data loggers were wired up and started. The reservoirs were filled with 50 mL of the particular water and the pumps were started. After checking for leaks and inspecting all the connections, the setup was moved to a dark room and the reservoirs topped up with 20 mL of the particular water. The water levels in the reservoirs were then marked and the reservoirs were kept filled to the same levels by topping up twice a week. Using peristaltic pumps, the circulation rate was maintained at about 150 mL/day.

The flow cell experiment was conducted for nine weeks. Upon termination, the reservoirs, tubing and flow cells and fresh or saline water rinses were drained into 100 mL glass bottles and the volume brought up to 100 mL with the Meech Lake or Tilt Cove water. The water samples were shipped back to the CANMET/MMSL for chemical analysis by ICP-MS for the fresh water leachates and chelation-ICP-MS for the saline water leachates as described above for the lysimeter samples. The thin sections were removed from the flow cells, rinsed with distilled water, dried and re-examined under a petrographic microscope to document any changes in mineral grain texture and morphology. The potential measurements made with the microelectrodes were downloaded from the data loggers and analyzed.

4.1.3 Batch leaching and sequential extraction analysis

To assess the extent of immediate contaminant release when tailings disposed on land at either site enter a new environment, selected samples of land-

disposed tailings from both sites were subjected to an 18-hour regulatory leach test according to the US-EPA1311 method. The method was modified such that fresh water from Meech Lake, Quebec, and seawater from Tilt Cove were used as the leach media. In addition to the overnight batch leach testing, sequential extraction analysis was conducted on 28 selected tailings and sediments from both sites at the Geological Survey of Canada, Ottawa. Using the procedure detailed by Hall et al. (1996), the analysis determined the partitioning pattern of 29 elements among seven major components of the geologic samples. The components considered include: 1) exchangeable ions, 2) carbonates, 3) manganese oxides, 4) amorphous iron oxyhydroxides, 5) crystalline iron oxides, 6) organics and sulfides; and 7) residual components (mainly silicates). Each successive leaching step reflects a greater difficulty for removal of the element concerned and hence its decreasing bioavailability

4.2 IMPACT ZONE DELINEATION

4.2.1 Hydroacoustic survey

The hydroacoustic survey was carried out under an independent contract by the Canadian Hydrographic Services, Department of Fisheries and Oceans. Details of the method can be found in Stirling and Roy (2000). Briefly, a shallow water EM 3000 multibeam acoustic survey was conducted at Little Bay and Tilt Cove. Horizontal and vertical datum were established and compared to historical data.

4.2.2 Trace elements in biota

4.2.2a Sample collection and analysis: Samples of mussels (*Mytilus edulis*), soft shell clams (*Mya arenaria*), seaweed (*Fucus anceps* and *Ascophyllum nodosum*), and sediment were collected at Little Bay, Tilt Cove, and a control site (Smith's Harbour) in August 1999 and June 2000. Mussels and clams were placed in clean seawater and allowed to depurate for 24 hours prior to freezing at –20°C. Bivalves were kept frozen until shucked in the laboratory. After shucking, the soft tissue of the bivalves was rinsed in ultra pure water (18MΩ) and dried to a constant weight at 80°C. Sub-samples of 8-10 individuals were pulverized and homogenized using a stainless steel grinder with stainless steel blades. Aproximately 0.3 grams of the homogenized material was digested using 0.3ml of trace clean concentrated nitric acid in a closed microwave digestion system. The temperature of the sample was raised to 150°C and held there for 15 minutes. One ml of the digested material was extracted and diluted to 50ml in ultra pure water and analyzed for Li, Mg, V, Cr, Mn, Co, Ni, Cu, Zn, As, Sr, Cd, Ba, Pb by ICP-MS.

Samples of seaweed were collected and placed in sterile whirlpac bags. Seaweed samples were placed in a cooler on ice until transported to the laboratory where they were stored at –20°C. To remove surface contamination, the seaweed was cleaned by removing any observed epifauna and by rubbing the surface of the

plants on a ridged plastic board. Care was taken not to rupture the walls of the plant stems or their bladders. Subsamples of plant material were dried to a constant weight at 80°C and pulverized by hand using an agate mortar and pestal. Approximately 0.5 grams of plant material was digested in a mixture of nitric acid and hydrogen peroxide (5ml to 3ml). A closed microwave system was used to bring the mixture to a temperature of 150°C and hold it there for 15 minutes. One ml of the digested material was extracted, diluted to 50ml using ultra pure water and analyzed for the same suite of elements as the bivalves above.

Quality control of the bivalve and seaweed analyses was monitored through the use of blanks, replicate analyses, and analyses of standard reference materials. Reported metals were judged to be within acceptable error limits.

4.2.2b Statistical analysis: The data from the analyses of the biota were examined to determine if there was a relationship between distance from the tailings and metal concentration in the biota. It was felt that a principal component analysis (PCA) was the most appropriate technique to assess such a relationship. The raw data was transformed using the equation 'new data = log(1+old data)'. The PCA was performed on the correlation matrix of the transformed data. Initially a PCA was performed on the mussel and seaweed data separately. However, the data sets were then merged and the PCA re-run to examine species effects.

4.2.3 Sediment collection and analysis

Sediment samples were collected using an Ekman grab. Once retrieved, the sediment sample was removed from the centre of the grab with a plastic scoop. Care was taken not to touch the sides of the grab and to avoid material in contact with the sides of the grab. The sediment was placed in sterile whirl pac bags and placed on ice. At the laboratory the sediment was stored at –20°C.

For chemical analysis, samples were removed from the bags using a plastic spatula, dried at room temperature under a clean fume hood, divided into coarse (>107 micron) and fine (<107 micron) fractions by sieving, and placed in acid washed plastic containers. Coarse fractions were powdered using an alumina ceramic mill. For X-ray fluorescence analysis, 3 g of sample powder were added to 0.42 g of BRP-5933 Bakelite phenolic resin binder (Bakelite Thermosets, Brampton, Ontario, Canada), mixed in a roller for 10 minutes, and pressed in a 29 mm diameter mould for 5 secs at a pressure of 20 tonnes. The pellets were dried in a 200°C oven for 15 min. Element data were collected using a Fisons/ARL model 8420+ sequential wavelength dispersive x-ray spectrometer.

For ICP-MS analyses, approximately 0.1 g of each sample was dissolved in 3 ml of nitric acid and 2 ml of hydrofluoric acid by heating to 180°C in a teflon screw top beaker for 16 hours. The solutions were evaporated to dryness, re-dissolved in 2 ml of nitric acid and 1 ml of boric acid, re-evaporated, and finally equilibrated in 2 ml of warm nitric acid, with 0.665 ml of boric acid and 1.35 ml of oxalic acid to ensure stabilisation of metals in solution. The solutions were diluted in 60 g of distilled water and, just prior to analysis for metals using a

Hewlett Packard 4500plus quadrupole ICP-MS, further diluted in distilled water. An internal standard solution of Sc, In and Re was used for matrix and drift correction. The same instrument was used to analyse the same solutions for Pb isotopes in a separate experiment. A spike of natural Tl was used for mass discrimination corrections. Background corrections in both the metal and lead-isotope experiments were made using blank acid solutions.

4.3 ECOTOXICOLOGY

4.3.1 Acute toxicity tests

Acute toxicity tests were carried out using standard Environment Canada protocols (Environment Canada 1990). Organisms tested included juvenile flounder (4 months old), trout larvae (4-6 months old), capelin larvae (1 month old), and mixed plankton samples.

4.3.2 Bivalve histopathology

4.3.2a Condition indices: Measurements of shell length, width, depth, soft tissue wet weight, dry weight, as well as, shell weight and cavity volume were taken to determine the general condition of mussels from Little Bay and the control site (Smith's Harbour). Shell length, width and depth were each measured as the maximum distance obtained using the unaltered (intact) organism. Wet weight was obtained by shucking each mussel and scraping all tissue into a weight boat, draining excess water and recording mass. Dry weight was the mass of the tissue recorded after 48 hours of drying at room temperature in a fume hood. The shell cavity volume was obtained by filling one of the valves level to the edges with fine-grained sand (100-250 µm) then pouring the contents into a graduated cylinder, multiplying the value by 2 and recording. Condition indices were calculated as a percentage of the tissue weight (wet and dry) versus shell weight with higher condition indices indicating healthier mussels (Grout et al. 1999). Condition indices were determined using 5mm size classes of the mussels which ranged from 30-35 mm to 90-95 mm.

4.3.2b Examination of clam hepatopancreas for abnormalities: Hepatopancreas samples were processed using standard histological methods (Lynch et al. 1969). Tissue was embedded in steel molds in molten embedding medium and allowed to cool. Sections, 6 microns thick were cut and mounted on clean slides. Sections were assessed microscopically for different lesions.

4.3.2c Examination of clam gills for abnormalities: Gill samples were processed using standard histological methods (Lynch et al. 1969). Gill tissue was then examined microscopically for evidence of abnormalities.

4.2.3d Examination of clam hemolymph for neoplasia: Neoplasia is a disease common to bivalves in polluted areas (McGladdery et al. 1993).

Hemolymph from *Mya arenaria* from Little Bay was examined for evidence of the disease. Hemolymph was withdrawn from the posterior adductor muscle with a syringe. A drop of hemolymph was placed on a Poly lysine slide and allowed to settle for 30 minutes. Cells were then dyed using Hema 3 stain. The number of neoplastic hemocytes were counted and the percent of abnormal cells was recorded. Animals were determined to be disease free if zero cells were abnormal. If there were greater than 80% abnormal cells then the animal was considered to be in the advanced stages of the disease. For more details on this method see Cooper et al. (1982).

4.3.3 Bivalve immunology

4.3.3a Phagocytosis: Phagocytized particles in hemocytes are an indication of an immune system response. It is assumed that if the immune system responds to exposure to a potentially toxic material, the exposure medium is precieved as a health risk to the organism. In vitro experiments were conducted by exposing mussel hemocytes to tailing leachates for 2 h before assessing immunological responses. Leachate exposure conditions for the phagocytosis assay are given in table 4.1. Leachates were prepared after mixing seawater with tailings for a few hours and allowing the mixture to settle for 24 h prior to filtration. The phagocytosis assay was conducted following La Peyre et al. (1995). Briefly, after exposure to the tailings leachate, 100 µl of hemolymph collected from the posterior adductor muscle of the mussels were placed onto a slide, and the hemocytes were allowed to settle for 30 minutes. Then, 40 µl of a zymosan suspension (1 mg/ml in seawater) were added to the hemocyte monolayer, and the slides were incubated for 45 minutes at room temperature in a humidified chamber. After two washes with seawater, the slides were stained with Hemacolor

Table 4.1. Lechate exposure parameters.

Grain size (G)	Amount of tailings used	Duration of exposure
250µm < G <500µm	9 g/L	2h
90µm < G <250µm	12.5 g/L	2h
75µm < G < 90µm	19	2h
Unsorted tailings	200 g/L	2h

and mounted with DePex. Counts of at least 100 cells were made for each individual or replica. The results were expressed as the percentage of phagocytic hemocytes or phagocytic rate (number of hemocytes with at least one zymosan particle/total number of hemocytes).

4.3.3b Serum protein levels: A second indication of an immune system response is increased protein levels in serum. Preparation of the leachate and the grain size categories for the serum protein experiment are the same as for the phagocytosis assay. Six mussels were exposed to each grain size leachate for seven days with the solution replaced every two days. After hemolymph collection, samples were centrifuged for 10 minutes at 4000 rpm and cells were

discarded. Serum samples were used to measure protein concentrations according to Lowry et al. (1951).

4.3.4 Oxidative damage

Oxidation of Cu can result in the production of free radicals through the Fenton Reaction. Free radicals are highly reactive species that can damage cell membranes, proteins, and DNA. Evidence of oxidative damage in biota suggests that damage is occurring as a result of chronic exposure. Two tests for evidence of oxidative damage are the thiobarbituric acid (TBA) test and the comet assay.

Samples of mussels and clams were collected in October 1999 at Little Bay and Smith's Harbour. In 2000, concern over size differences between clams at Little Bay and Smith's Harbour led to the addition of a second control site at Swift Current, Trinity Bay. Samples from each site were kept alive, packed in seaweed and held in coolers on ice as they were transported to the lab. At the laboratory the animals were placed in seawater in separate aquaria per site in seawater. Tissue samples for biochemical analysis were taken within 48 hours of arrival at the laboratory.

4.3.4a Lipid peroxidation: Tests were conducted on clams collected from Little Bay, control sites, and those exposed to tailings leachate (200 g/L, 7 days, solution replaced 4 times). Lipid peroxidation in gill and hepatopancreas samples was monitored by measuring the concentration of thiobarbituric acid reactive species (TBARS) as described by Uchiyama and Mihara (1978). In a 10 ml test tube, 0.5 ml of S9 was mixed with 3 ml of 1% H_3PO_4 to keep the pH of the medium at about 2.0. One ml of 0.6% aqueous TBA was then added and the mixture was heated at 100°C for 45 min. After cooling, 4 ml of 1-butanol was added and the mixture was shaken vigorously. The butanol phase was separated by centrifugation and its absorbance at 535 and 520 nm was measured. The difference in absorbance at these two wavelengths was taken to avoid interference due to protein. Tetramethoxypropane was used as an external standard. The level of TBARS is expressed as nmol/mg protein.

Enzyme activities were measured using S9 samples of both gills and hepatopancreas of clams and mussels. The activity of NADPH cytochrome c reductase (CYT RED) was determined by monitoring the increase in absorbency at 550 nm using an extinction coefficient of 21 $mM^{-1}.cm^{-1}$ for reduced cytochrome c (Masters et al. 1967). The activity is expressed in nmol/min/mg protein. Catalase activity was measured according to Greenwald (1985) and expressed as µmol/min/mg.

4.3.4b Comet assay: The Comet assay (Steinert et al. 1998) was performed on hemocytes and digestive gland cells of clams collected from Little Bay and Swift Current in November 2000. Hemolymph was withdrawn from adductor muscles using a 25 gauge needle attached to a 1 ml syringe. Immediately following collection, hemolymph samples (0.5 ml) were transferred to microfuge tubes and centrifuged for 2 min using a table top centrifuge to pellet cells (7000g).

Digestive glands were excised from each animal and cells isolated by non-enzymatic tissue dissociation. The use of trypsin for cell disagregation was omitted due to increase in the % DNA in the tail with this enzyme (Birmelin et al. 1998). The glands were dissociated by stirring tissue pieces (1g/25 ml) in a buffer containing 20 mM Hepes, 500 mM NaCl, 12.5 mM KCl and 5 mM EDTA (1100 mOsm) for 1 hour. The number of cells and their viability was evaluated by Trypan blue exclusion. After dissociation, the cell suspension was filtered through a 200 µm filter and 1.5 ml of the filtrate was transferred to Eppendorf tubes for centrifugation (300g, 10 minutes).

Cells (hemocytes or digestive gland cells) were suspended in 250 to 500 µl of warm 0.5% low melting agarose in Kenny's solution (0.4M NaCl, 9 mM KCl, 0.7 mM K_2HPO_4 and 2 mM $NaHCO_3$, pH 7.5) for hemocytes and in a physiological saline solution (1100 mOsm, pH 7.3, containing 20 mM Hepes, 436 mM NaCl, 10 mM KCl, 10 mM $CaCl_2$, 53 mM Mg SO_4, pH 7.3) for digestive gland cells. The volume of agarose was dependent upon the size of the cellular pellet; larger pellets of digestive gland cells were obtained and resuspended in larger volumes. A 100 µl aliquot of the cell suspension was then transferred onto slides previously coated with 0.5% normal melting agarose in the same buffers. After gelling, the slides were placed in lysing solution (2.5 M NaCl, 10 mM Tris, 0.1 M EDTA, 1% sarcosyl, 1% Triton X-100 and 10% DMSO, pH 10.0) in glass Coplin jars and incubated at 4°C for at least 2 h. After incubation, slides were transferred to clean Coplin jars filled with distilled water and rinsed twice. The slides were then placed in a submarine gel electrophoresis chamber filled with 300 mM NaOH, 1 mM EDTA and the DNA was allowed to unwind under these conditions for 30 minutes. After unwinding, the samples were subjected to electrophoresis at 25 V for 15 minutes. The slides were neutralized with 2 rinses in 0.4 M Tris and DNA stained with 50 µl of a 20 µg/ml solution of ethidium bromide in distilled water. Slides were observed using a fluorescence microscope system and ocular micrometer. The total length of the DNA migration was then measured for 15-40 cells per slide.

4.3.5 Neuroendocrine effects

To determine if there were any potential effects on the neuroendocrine system, trout were exposed to tailings leachate. Solutions were produced by mixing 250 g of tailings with clean water and shaking. Trout were exposed to the leachate for 48 hours. Evidence of a change in skin pigmentation was determined by observing the trout from above against a white background.

4.3.6 Short term toxicity tests

4.3.6a Microtox®: Microtox® Large sample Procedure (Microbics Corporation 1992; AZUR Environmental 1999) is based on suppression of the bioluminescence evolved by the marine bacterium *Vibrio fischeri* on exposure to toxicants. Sediment samples were mixed with Solid Phase Test Diluent to prepare

a test solution. Toxicity was expressed as the effective concentration of the test solution that induces a 50% reduction in bioluminescence relative to a control.

4.3.6b Amphipod survival and polychaete survival and growth: Amphipod survival tests were conducted according to Environment Canada (1998) protocols using the marine amphipod *Rhepoxynius abronius*. All test parameters were maintained within the recommended levels outlined in the protocol.

Polychaete survival and growth were carried out using *Neanthes arenaceodentata*. Survival tests followed the protocols of Environment Canada (1998). Growth was based on weight gain and measured in mg/day. Animals were exposed to 100% tailings or a mixture of 15% tailings and 85% control sediment. Tests were conducted over a 20 day period.

4.3.7 Avoidance behaviour

Hatchery-reared juvenile winter flounder (2 +) obtained from the Ocean Sciences Centre, Memorial University of Newfoundland, were used to determine if the fish avoided a tailings substrate. Fish were held in 1 m^2 tanks with ambient sea water (mean temperature ± SE, 12.1 ± 0.02 °C), and were fed commercial pellets once per day ad libitum. The mean standard length of the test fish was, 8.8 ± 0.2 cm.

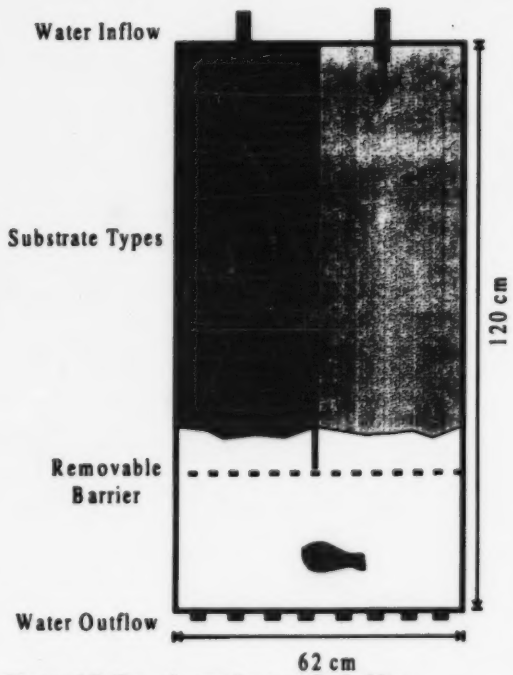

Figure 4.2. Experimental set-up for habitat avoidance tests.

The two-choice test tank measured 120 x 62 x 30 cm with a dividing wall running 90 cm lengthwise down the centre. A perforated removable barrier was placed at the end of the dividing wall creating an acclimation area (Fig. 4.2). Water was fed directly into each alley of the test tank at approximately 2 L/min. Outflow holes at the end of the test tank maintained a water level of 20 cm. The water temperature of the test tank was equal to the holding tanks.

Fish were tested in two trial configurations: (1) tailings (Little Bay) versus control sediment (Hutcheson Sand and Gravel Ltd., Ontario) and (2) tailings versus natural substrate. The proportion of grain sizes in each substrate type are displayed in Table 4.2. The substrate types required for each trial

configuration were placed in the alleys of the test tank and allowed to settle for 24 hours. The depth of the substrate in the alleys was approximately 4 cm. A fish was placed in the acclimation area of the test tank for 1 hour. After this time the removable barrier was lifted allowing the fish access to the two-choice alleys. The

Table 4.2 Analysis of dry sediments

	Proportion of sample (%)		
Particle size (μm)	Copper mine tailing	Control	Natural
> 250	48.8	4.1	94.3
75 - 250	39.0	30.8	4.9
< 75	12.2	65.1	0.8

fish was barrier was lifted allowing the fish access to the two-choice alleys. The fish was recorded using a video camera and time-lapse VCR for 21 to 22 hours. Twenty fish were tested in each trial configuration. Each fish was only tested once. The substrate type in each alley was switched midway through each configuration to eliminate any preference the fish may have for a particular side of the test tank.

To test if fish preferred one substrate type over another, the proportion of time spent in each of the two-choice alleys was compared with a random distribution of time spent in either alley using a Wilcoxon's matched-pairs signed-ranks test.

4.3.8 Benthic community structure

Benthic organisms from three sediment samples were collected by passing sediment through a 0.5mm sieve. Collected organisms were stored in 70% isopropyl alcohol. Counting of individuals and sorting into species was carried out under a low power (8X) dissecting microscope.

5 RESULTS

5.1 CHEMICAL ASSESSMENT

5.1.1 Site assessments and observations

Both the Tilt Cove and Little Bay sites hosted massive sulfide and related deposits enriched in copper as chalcopyrite. At Tilt Cove, the host rocks for the ore bodies are highly chloritized, sheared and brecciated andesitic pillow-lavas and agglomerates. Fine-grained pyrite and chalcopyrite are the chief components of the mineralization, which also includes minor pyrrhotite, sphalerite and locally some magnetite. At Little Bay, mineralization consists of pyrite, chalcopyrite, pyrrhotite and magnetite as well as minor wurtzite and marcasite in echelon zones of chlorite schist in altered, basaltic pillow-lava, aquagene tuffs and agglomerates. Quartz, epidote, chlorite and minor calcite are the principal gangue minerals

As evidenced by the formation of acidic efflorescent salts on exposed, mineralized rock fragments, the fine-grained pyrite at Tilt Cove is highly reactive. Relatively fresh bulk tailings sampled from beneath a ball-field gave a paste pH of 4.1 and the overlying oxidized material a paste pH of 2.7. However, some gangue minerals associated with the sulfide mineralization contain sufficient neutralization capacity to provide a local, near-neutral pH environment for the perseverance of malachite on the ground surface. The heterogeneity in mineral distribution is also reflected in water chemistry. The pH of the discharge from the closed shaft ranges from 3.4 to 5.9 depending on the season of sampling while that of pit water in the West Mine varies from 7.1 to 7.5.

Although the Little Bay tailings are finer than those found at Tilt Cove (mean grain size of 21.9 μm versus 50.8 μm), they are much less reactive possibly because the contained sulfides are more euhedral and coarser-grained than those at Tilt Cove. Visible evidence of surface oxidation (i.e., intensive iron staining) has only been observed at the western end of the tailings deposit, especially at the toe adjacent to the running stream, and at the perimeter of the impoundment where influx of surface runoff is evident. Seepage from the toe of the tailings deposit at its western extremity is acidic (pH as low as 3.4). However, malachite is occasionally observed in waste rock piles uphill of the tailings impoundment, again reflecting the heterogeneous composition of the mine waste. Progressing towards Little Bay Arm, water in the stream incising the tailings deposit in the east-west direction exhibits increasing pH, conductivity as well as chloride and sulfate contents, suggesting increasing influence of saline water from the Arm.

5.1.2 18-hour leach test

The results from the 18-hour leach test are presented in Table 5.1. The saline water leach enhanced the release of Pb, Ni and Zn, but had no obvious effect on Cu concentrations.

Table 5.1. Results of the 18-hr leach test using fresh and saline water as leach media. LB represents Little Bay samples. TC represents Tilt Cove samples.

Sample Description	Fresh Water Leachate	Saline Water Leachate
LB20-1, low grade ore	pH 3.3	pH 3.8
Cu, mg/L	26.7	32.7
Ni, µg/L	80.8	131
Pb, µg/L	1.28	24.1
Zn, µg/L	421	547
LB22-3b, oxidized tails	pH 3.5	pH 4.2
Cu, mg/L	2.51	1.87
Ni, µg/L	42.3	57.6
Pb, µg/L	<1	2.54
Zn, µg/L	119	173
LB-bulk tailings	pH 7.6	pH 7.3
Cu, mg/L	0.007	0.074
Ni, µg/L	0.92	15.9
Pb, µg/L	<1	2.23
Zn, µg/L	3.2	4.0
TC23a, oxidized tails	pH 3.0	pH 3.4
Cu, mg/L	0.632	0.612
Ni, µg/L	51.5	73.5
Pb, µg/L	4.89	27.8
Zn, µg/L	235	470
TC23b, oxidized tails	pH 2.9	pH 3.1
Cu, mg/L	1.23	1.61
Ni, µg/L	144	189
Pb, µg/L	2.35	11.3
Zn, µg/L	621	841
TC-bulk tailings	pH 4.6	pH 5.2
Cu, mg/L	9.57	9.66
Ni, µg/L	91.1	128
Pb, µg/L	35.4	54.5
Zn, µg/L	1705	2184

5.1.3 Sequential extraction analyses

At Tilt Cove and Little Bay the partitioning of the metals varied with the source of the material (marine or on-land) and the oxidation state (oxidized or non-oxidized). Marine sediments were distinct from on-land tailings and oxidized surface samples were distinct from un-oxidized samples collected from depth. A detailed interpretation of the sequential extraction data will be fully documented in a separate paper (Kwong et al. in preparation). For this section of the report only the extraction results on Cu, Pb, Zn, and Ni are summarized.

At Tilt Cove, the majority of Cu in the on-land and marine tailings are bound in sulfides (70-80%). A significant amount of Cu is associated with crystalline iron oxides in the tailings found on land, and with carbonates in the marine sediment. Appreciable amounts of exchangeable Cu (5%) is found only in the un-oxidized tailings sample (Fig. 5.1). Seventy-five to 80% of Pb in the Tilt

Cove tailings occur as sulfides with the remainder partitioned among the iron and manganese oxides and oxyhydroxides as well as the carbonate fractions. In contrast, in the marine sediment, 40% of Pb occurs as sulfides, 40% associated with iron oxyhydroxides and the remainder divided among the manganese oxide, crystalline iron oxides, carbonate and the residual fractions. The majority of Zn in the tailings occurs as sulfides (70-90%) and the remainder is mainly bound by crystalline iron oxides. In the marine sediment, however, 60% of Zn occurs as sulfides, 20% resides with the residual fraction and the remainder fractionated among the crystalline and amorphous iron oxides, manganese oxide, and carbonate fractions. The partition pattern for Ni is similar for both the on-land tailings and the marine sediment. 60-70% of Ni is bound in sulfides, 20-25% in the residual fraction and the remainder largely rests with crystalline iron oxides. In the marine sediment, however, about 5% of Ni is also bound with carbonate.

At Little Bay, the majority of Cu occurs as sulfides in the on-land tailings (45-85%), however, increasing proportions of Cu are bound in other forms when Little Bay Arm is approached (Fig. 5.2). Thus, in the five marine sediments analyzed, only 25-35% of Cu occurs as sulfides, 35-40% is carbonate-bound, 10-15% with manganese oxides and the reminder largely associated with amorphous and crystalline iron oxides and oxyhydroxides.

With Pb the partition pattern is erratic in the on-land tailings. Major hosts include the residual fraction (15-65%), organics and sulfides (15-55%), amorphous iron oxyhydroxides (10-25%), crystalline iron oxides (5-20%) and manganese oxides (≤5-20%). In the bay sediments, the Pb distribution is more uniform. Thirty-40% of Pb is bound in amorphous iron oxyhydroxides; 25-30% with the residual fraction, 15-20% with manganese oxides, ≤5-20% with the sulfides, and about 10% with crystalline iron oxides. Exchangeable and carbonate Pb are insignificant.

Both the concentration and the partition pattern do not differ much between the on-land tailings and bay sediments for Zn and Ni. Forty-55% of Zn is bound in the residual fraction, 25-40% with sulfides and the remainder divided among the iron and manganese oxides and oxyhydroxides as well as the carbonate fractions. In the sediments, the residual fraction uniformly accounts for 55% of Zn and the organics and sulfides 20%. For Ni in the tailings on land, 25-60% is bound with organics and sulfides, 30-55% with the residual fraction and the remainder divided among the iron and manganese oxides and carbonate species. In the bay sediments, the residual fraction accounts for 45-50% of Ni, organics and sulfides 25-30%. Both exchangeable Zn and Ni are insignificant by proportion in the tailings on land and sediments in Little Bay Arm.

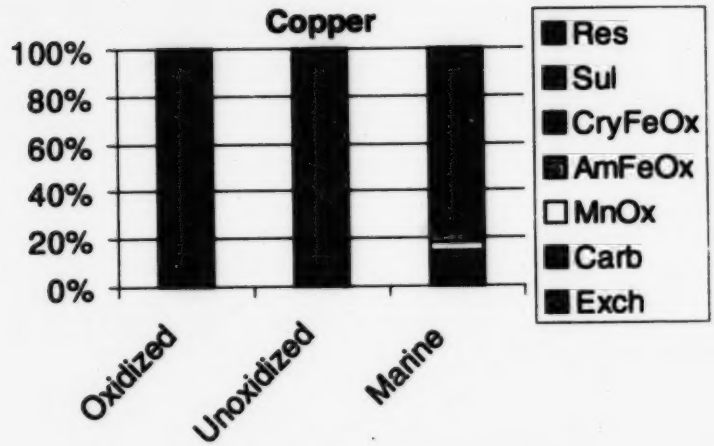

Figure 5.1. Partition pattern for Cu in Tilt Cove tailings.

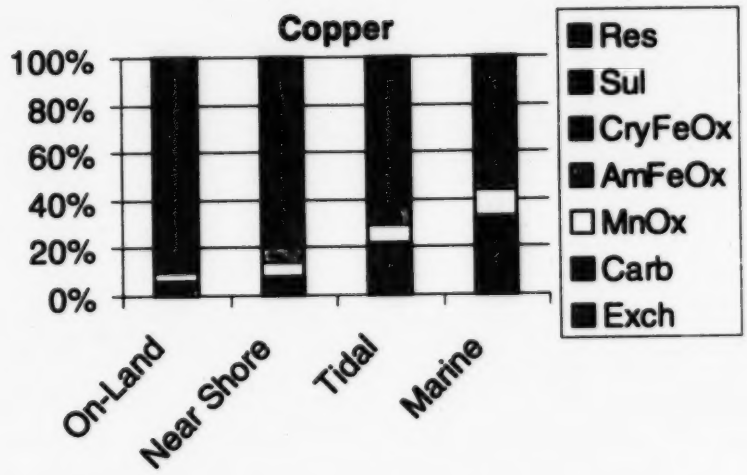

Figure 5.2. Partition pattern for Cu in Little Bay tailings.

5.1.4 Galvanic interactions

Petrographic examination of the polished thin sections at the end of the nine-week experiment showed clear evidence of preferential weathering (tarnishing or dissolution) of minerals with a lower electrode potential (e.g., pyrrhotite, galena, and chalcopyrite) in contacting sulfide pairs. The extent of weathering in many cases appears to be more intensive in the saline medium than fresh water. The leaching of Cu, Ni, Pb and Zn from the specimens is shown in Table 5.2.

Table 5.2. Concentrations of metals measured in fresh and saline mediums at the end of the galvanic interaction experiment.

Sample Description	Fresh Water	Saline Water
LB-1 with chalcopyrite-pyrrhotite pair		
Cu µg/L	5.0	29
Ni µg/L	0.35	4.0
Pb µg/L	<1	2
Zn µg/L	3.1	13
LB-2 with pyrite-chalcopyrite pair		
Cu µg/L	12	14
Ni µg/L	0.09	0.70
Pb µg/L	<1	<2
Zn µg/L	1.5	0.3
TC-1 with pyrite-chalcopyrite pair		
Cu µg/L	34	54
Ni µg/L	0.36	0.75
Pb µg/L	<1	<2
Zn µg/L	4.5	0.3
TC-2 with pyrite-chalcopyrite pair		
Cu µg/L	8.3	7.4
Ni µg/L	4.8	8.1
Pb µg/L	<1	<2
Zn µg/L	0.59	<0.5
Onek-1with pyrite-sphalerite-galena		
Cu µg/L	<0.5	<0.5
Ni µg/L	0.09	<0.1
Pb µg/L	62	440
Zn µg/L	29	11

Data presented in Table 5.2 clearly demonstrates that the mobility of Pb in sample Onek-1 is enhanced in a saline environment, possibly due to the formation of lead chloride complexes. Ni leaching also appears to be enhanced under a saline water cover but the data for Cu and Zn are inconclusive.

It should be noted that the galvanic interaction experiment was conducted under conditions of a fully oxygenated shallow water cover (3-4 mm). In an oxygen-depleted system such as sulphidic tailings beneath organic debris in a natural lake or on the seafloor, galvanic interaction will be suppressed (John Kwong pers. comm.). Thus preliminary measurements of metal flux from the Tilt Cove tailings using the technique of diffusion gradient in thin films provided

evidence that the submerged tailings behaved as a sink instead of a source of the base metals.

5.1.5 Lysimeter studies

The bulk chemical and mineralogical compositions of the Little Bay and Tilt Cove tailings are given in Tables 5.3 and 5.4, respectively. The Little Bay Tailings were low acid-generating, having a total sulphur content of ~ 1.5 – 2.0%, and a net neutralization potential (NNP) of approximately –45 kg $CaCO_3$/tonne.

Table 5.3. Bulk chemical compositions (Wt.%) of the Little Bay and Tilt Cove tailings.

	TC Bulk	LB Bulk
Al	5.6	6.1
As	0.03	<0.01
C	0.123	0.172
Ca	1.3	1.9
Cu	0.4	0.04
Fe	30.1	13.8
K	<0.3	<0.3
Mg	3.2	3.7
Mn	0.051	0.13
Na	0.07	0.65
Ni	0.02	0.008
S_{total}	18.72	1.726
Si	8.16	23.51
SO_4	3.18	0.31
Ti	0.22	0.29
Zn	0.39	0.01

The Tilt Cove tailings were highly acid-generating, having a much higher total sulphur content of between 18 and 20%, and NNP of –534 kg $CaCO_3$/tonne.

The surface and porewater quality results for pH, total acidity, and dissolved concentrations of sulphate, total iron, calcium, copper, lead and zinc are summarized below

5.1.5a Little Bay Tailings – Fresh Water Cover: The Little Bay tailings under a fresh water cover showed very little to negligible acid generation and release of contaminants to the surface water cover (Fig. 5.3). The surface water pH remained nearly neutral to slightly alkaline (pH 7-8), throughout the 1.5 year monitoring period. The total acidity decreased from an initial high value of ~120 mg $CaCO_3$/l to zero in approximately the first 50 days, and the total alkalinity increased to ~60 mg $CaCO_3$/l during this period. Both dissolved SO_4 and Ca concentrations showed an increasing trend with time, resulting from the diffusion of dissolved gypsum ($CaSO_4.2H_2O$) from the near surface, shallow zone porewater of the underwater deposited tailings. The concentrations of dissolved total iron, Cu, Ni, Zn, Pb and other metals were low or near detection levels in the surface water column.

5.1.5b Little Bay Tailings – Saline Water Cover: Similar to the fresh water cover scenario, the Little Bay tailings under a saline water cover showed very little to negligible surface reactivity and the associated release of acidity and dissolved metal contaminants (Fig. 5.4). In this case, because of the available alkalinity of the sea water, the surface water pH remained slightly alkaline at ~ 8, the total acidity quickly decreasing from an initial low level of ~10

Table 5.4 Mineralogical compositions of the Little Bay and Tilt Cove tailings.

Tilt Cove Tailings		Little Bay Tailings	
Mineral	Wt. %	Mineral	Wt. %
Quartz	2.2	Quartz	28.8
Plagioclase	0.3	Plagioclase	6.4
Muscovite	0.6	Mica	0.9
Amphibole	tr	Amphibole	3.0
Rutile	0.3	Titanite	1.5
Gypsum	2.5	Gypsum	0.2
Epidote	0.1	Epidote	6.5
Clinchlore	36.3	Clinchlore	40.3
Fe Sulfates	0.4	Fe Sulfates	nil
Siderite	0.5	Siderite	2.2
Fe oxyhydroxides*	nil	Fe oxyhydroxides*	nil
Ilmenite	0.5	Ilmenite	0.1
Goethite	tr	Goethite	0.2
Magnetite	8.6	Magnetite	1.1
Pyrite	45.1	Pyrite	7.8
Pyrrhotite	0.2	Pyrrhotite	tr
Chalcopyrite	1.3	Chalcopyrite	0.2
Sphalerite	1.1	Galena	tr
		Calcite	0.8
Total	100.0		100

*Not including Goethite tr = trace nil= not detected

mg $CaCO_3$/l to zero, and total alkalinity remaining nearly constant at ~100 mg $CaCO_3$/l. An increasing trend in dissolved SO_4 and Ca concentrations in the surface water column was also seen in this case, resulting from gypsum dissolution and release from the tailings substrate. Slightly elevated concentrations of dissolved total iron, at 1-5 mg/l level, were also observed in the surface water column, however, the origin and chemical speciation is not fully understood at the observed alkaline pH conditions and needs to be further investigated. The concentrations of other metals were low or near detection levels.

The underwater deposited tailings substrates in both cover conditions showed some dissolved oxygen consumption, but the extent of any surface oxidation occurring at the tailings-water interface cannot be ascertained from the observed water quality results. Perhaps, the rate of oxidation is too low in this case and a complete acid neutralization is provided by the available alkalinity in the tailings substrate. Formation of an iron hydroxide precipitation layer at the

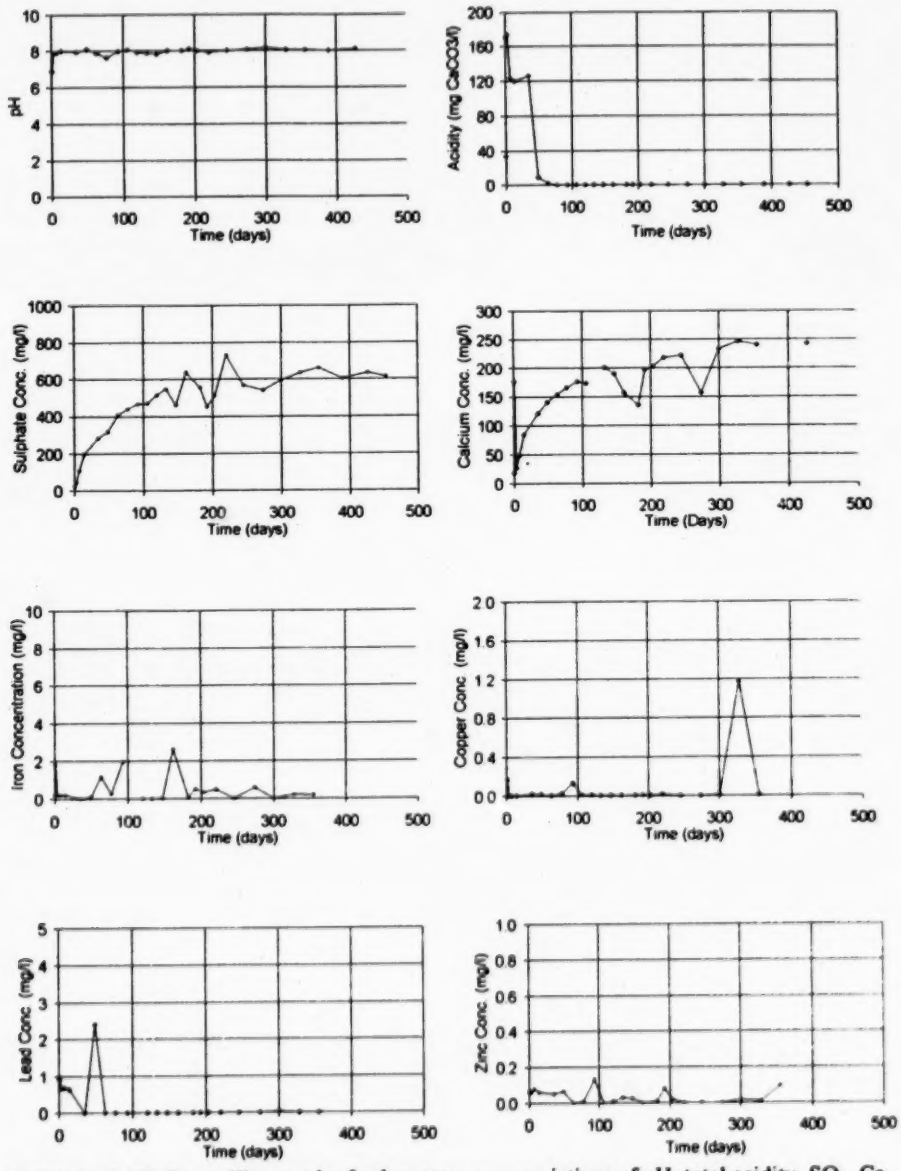

Figure 5.3 Little Bay tailings under fresh water cover; variations of pH, total acidity, SO_4, Ca, Fe total, Cu, Pb, and Zn in the surface water column over time.

tailings surface, common to underwater deposited reactive tailings, was absent in these tailings under both cover conditions.

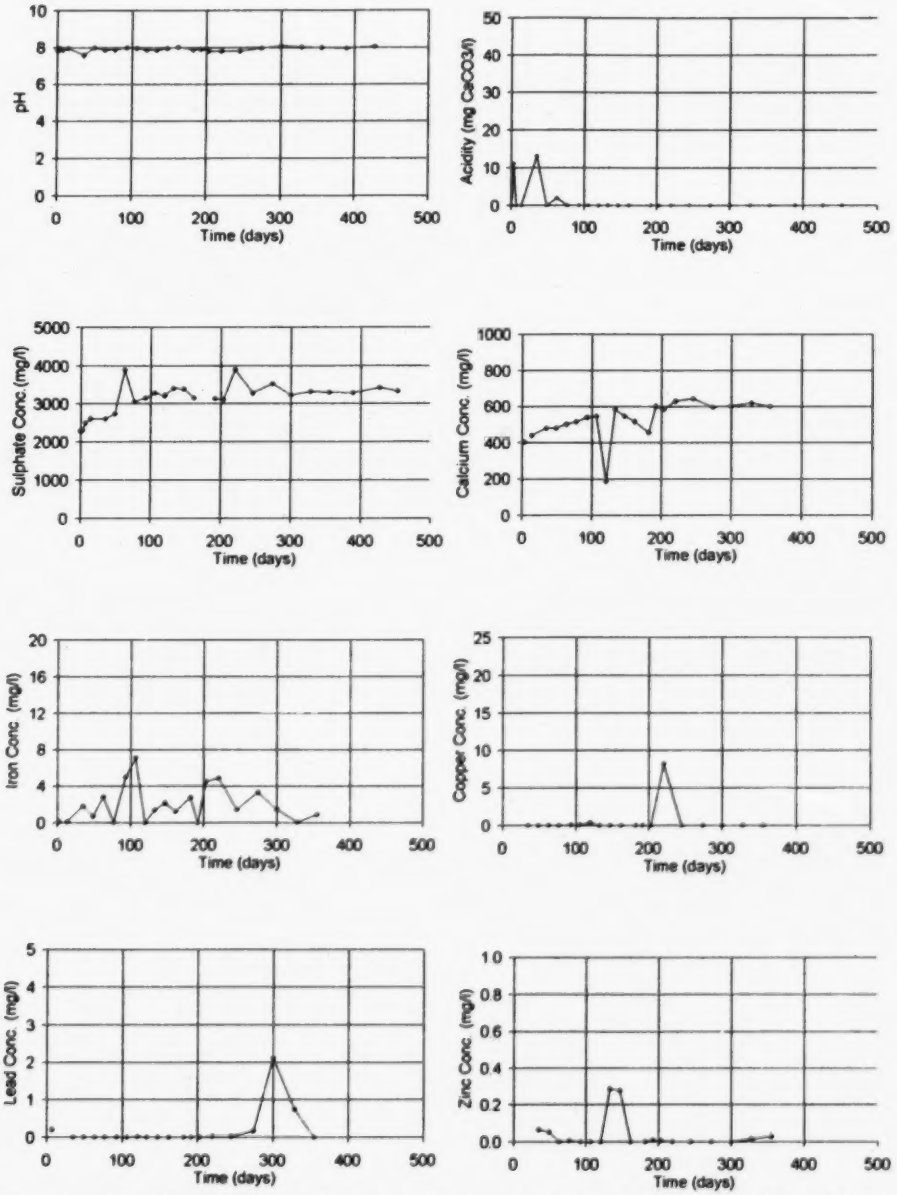

Figure 5.4. Little Bay tailings under saline water cover; variations of pH, total acidity, SO_4, Ca, Fe total, Cu, Pb, and Zn in the surface water column over time.

5.1.5c Tilt Cove Tailings – Fresh Water Cover: In contrast to the Little Bay tailings, the high sulphide-containing Tilt Cove tailings showed significant reactivity under both cover conditions. For the fresh water case (Fig. 5.5), the surface water pH decreased within the first 35 days to ~ 4.0, decreasing gradually

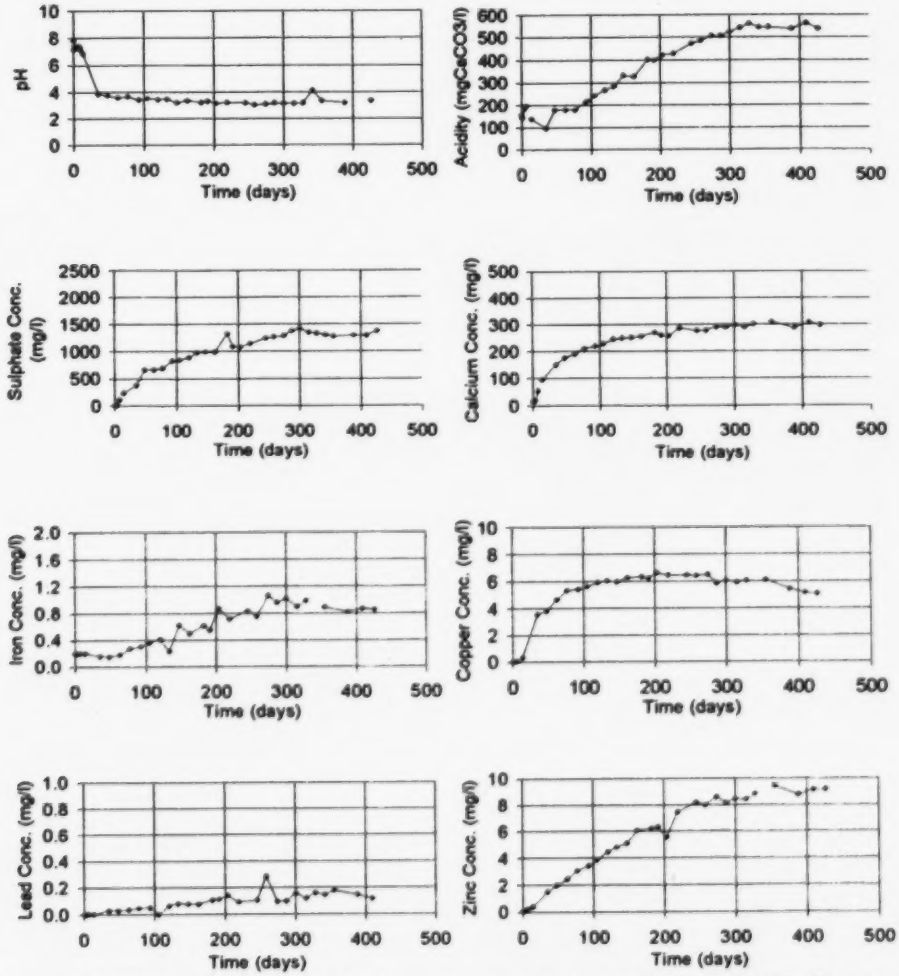

Figure 5.5. Tilt Cove tailings under fresh water cover; variations of pH, total acidity, SO_4, Ca, Fe total, Cu, Pb, and Zn in the surface water column over time.

thereafter to ~ 3 during the rest of the monitoring period. The total acidity of the surface water increased from ~ 100 mg $CaCO_3$/l at the start to ~ 550 mg $CaCO_3$/l by the end of the study. The total alkalinity decreased quickly from an initial 35 mg $CaCO_3$/l to zero, rendering the surface water column acidic thereafter. The dissolved SO_4 and Ca concentrations increased, respectively, from a low level of 10 mg/l to ~ 1300 mg/l and zero to 300 mg/l. With decreasing pH, the

concentrations of total iron in the surface water increased from ~ 0.2 to 1 mg/l, copper from nearly zero to ~ 6 mg/l, lead from nearly zero to ~ 0.2 mg/l, zinc from zero to ~ 9 mg/l and aluminium from nearly zero to 80 mg/l. A thick layer of iron hydroxide precipitate formed at the surface of the underwater deposited tailings and on the walls of the lysimeter during the monitoring period.

The porewater in these tailings had a low acidic pH of ~ 4, and contained high total acidity and dissolved concentrations of Fe, SO_4, Ca and Zn,

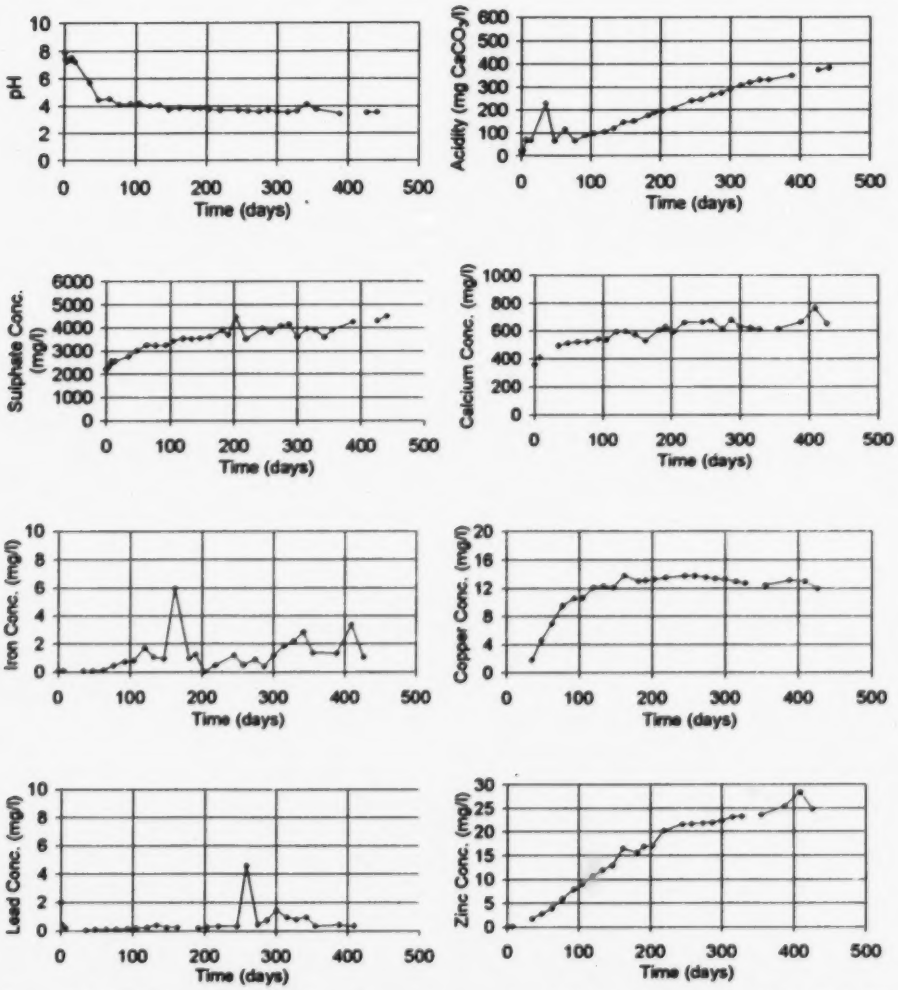

Figure 5.6. Tilt Cove tailings under saline water cover; variations of pH, total acidity, SO_4, Ca, Fe total, Cu, Pb, and Zn in the surface water column over time.

respectively, at 500 mg $CaCO_3$/l, 300 mg/l, 500 mg/l and 8 mg/l. There was a significant release of iron and other dissolved metals from the tailings porewater to the overlying surface water column. However, the formation of the iron

hydroxide layer at the surface of the tailings controlled, to a certain extent, the surface water concentrations of these diffusing species.

5.1.5d Tilt Cove Tailings – Saline Water Cover: Similar to the fresh water cover condition, the Tilt Cove tailings under saline water also showed significant surface reactivity and release of contaminants from surface oxidation and dissolution of previously accumulated oxidation reaction products (Fig. 5.6). The surface water pH decreased from an initial high value of ~ 8 to ~ 3.5, total acidity increased from ~ 75 mg $CaCO_3$/l to 380 mg $CaCO_3$/l, and total alkalinity decreased rapidly from an initial high of 100 mg $CaCO_3$/l to zero within the first 50 days. The results showed increased release of SO_4, Fe, Ca, Cu, Al, Pb, Zn and other metals to the surface water column. There was no appreciable difference between the fresh and saline water cover conditions, except the available high alkalinity of the sea water delayed the acid generation and metals release in the latter case. A thick layer of iron hydroxide precipitate also formed at the surface of the underwater deposited tailings and on the walls of the lysimeter during the monitoring period.

5.2 IMPACT ZONE DELINEATION

5.2.1 Hydroacoustic survey

Detailed results of the acoustic survey carried out at Little Bay and Tilt Cove can be found in Stirling and Roy (2000) including false coloured bathymetric images, backscatter images, and a detailed comparison of historical and new multibeam data sets. Briefly, Little Bay Arm (refer to Fig. 2.2) is a well protected southwest to northeast trending fjord-like feature with an eastern and a western basin. Emanating from the entrance to Shoal Arm, and extending eastward, downslope, into the east basin is a trench-like feature. The trench is believed to be indicative of the transport of large amounts of mine tailings from the on-land tailings disposal site. It is calculated that 500,000 m^3 of tailings have been deposited in Little Bay Arm with the bulk of it ending up in the deeper part of the east basin. A comparison of the historical data with the current multibeam data confirms that large amounts of material have been deposited in the east basin (Fig. 5.7).

The Tilt Cove site (refer to Fig. 2.3) is a dynamic coastal area that has been described by the Shaw et al. (1999) study, as having a "wave and current dominated zone" with a transition to an "iceberg impacted zone" further offshore. This section of the coastline is exposed to the full wave action of the sea, resulting in a constant scouring of the exposed bedrock seafloor, with deposition of scoured material occurring in the depressions between areas of bedrock highs. Despite the energy regime of the site, the acoustic survey found evidence of tailings immediately south and west of the entrance to Tilt Cove Harbour. A comparison of historical and recent acoustic data illustrates large differences in the seafloor profile (Fig 5.8). The differences in bathymetry are greater than that expected from natural erosion and deposition.

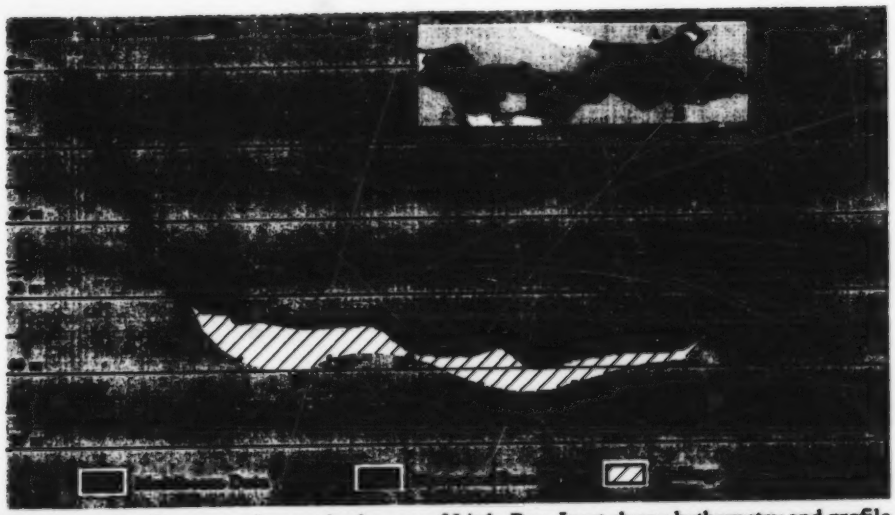

Figure. 5.7. Profile across the east basin area of Little Bay. Inset shows bathymetry and profile location. Images produced by and used with permission of the Canadian Hydrographic Service and the University of New Brunswick Ocean Mapping Department

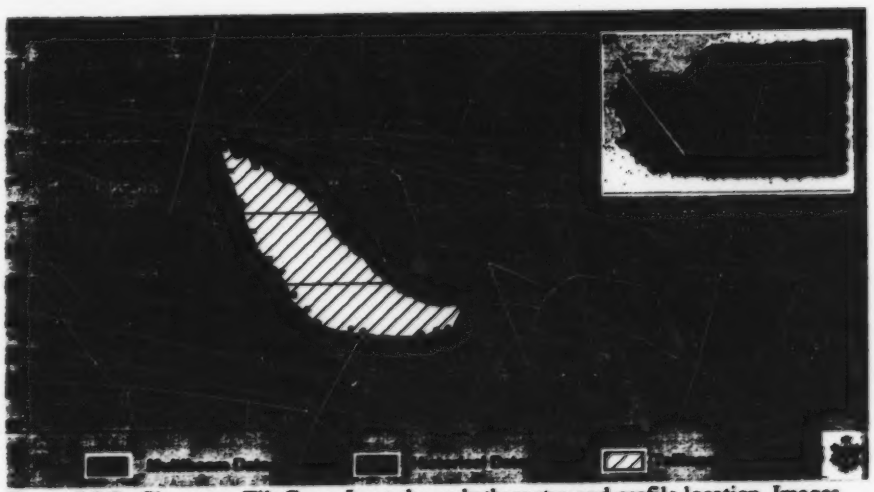

Figure 5.8 Profile across Tilt Cove. Inset shows bathymetry and profile location. Images produced by and used with permission of the Canadian Hydrographic Service and the University of New Brunswick Ocean Mapping Department

5.2.2 Composition of on-land and marine tailings

The major element composition of on-land tailings at Tilt Cove are distinctly different from samples taken 500 m from shore (Table 5.5). The marine sediments are depleted in Fe and S (the main constituents of the predominant minerals at the site) relative to the tailings on land. However, the marine

sediments are enriched in Fe and S relative to the control site. This suggests that the sediment at Tilt Cove is a mixture of tailings and natural sediments.

In contrast, the major element composition of on-land tailings and marine sediment at Little Bay are very similar (Table 5.5). Both on-land and marine

Table 5.5. Major element composition of Tilt Cove and Little Bay tailings.

	Tilt Cove		Little Bay		Control
	On-Land	Marine	On-Land	Marine	Marine
SiO2	16.41%	32.72%	42.24%	43.28%	55.59%
TiO2	0.43%	0.56%	0.49%	0.49%	0.34%
Al2O3	7.87%	9.48%	9.23%	11.84%	9.53%
Fe2O3T	39.14%	26.66%	20.96%	23.49%	3.14%
MnO	0.07%	0.13%	0.25%	0.24%	0.04%
MgO	4.89%	7.42%	8.11%	10.54%	1.71%
CaO	1.02%	4.94%	2.63%	2.25%	2.07%
Na2O	0.11%	1.18%	0.50%	0.77%	4.49%
K2O	0.13%	0.74%	0.08%	0.13%	1.77%
P2O5	0.04%	0.14%	0.03%	0.06%	0.11%
S	12.24%	6.74%	0.97%	0.68%	0.26%
Cl	0.01%	0.97%	0.01%	0.47%	1.65%
OH	n.a.	n.a.	n.a.	n.a.	n.a.
CO3	n.a.	n.a.	n.a.	n.a.	n.a.
Total	82.3%	91.6%	85.50%	94.26%	80.7%

tailings have large concentrations of SiO_2 and total iron (Fe_2O_3). This is consistent with the mineralogy of the deposits, which indicate that quartz and clinochlore are the most abundant minerals present. Sulphide minerals are a minor component of both on-land and marine tailings, which is reflected in the low S contents of the bulk samples.

The trace element content of the two sites follows trends similar to the major elements (Table 5.6). At Tilt Cove the trace metals in the sediment are unevenly distributed and, with the exception of a few sites near shore, depleted in Cu, Zn and Pb relative to the tailings on land. The distribution of the Cu in the sediment suggests that material is being transported along the shore in a south westerly direction (Fig. 5.9).

Table 5.6. Trace element composition (ppm) of Tilt Cove and Little Bay tailings.

	Tilt Cove		Little Bay		Control
Element	On-Land	Marine	On-Land	Marine	Marine
Cu	3500	810	450	350	16
Mn	500	1175	1500	1565	1022
Ni	200	180	79	76	42
Zn	2300	753	140	125	72
As	180	208	50	105	6
Pb	115	31	3	6	34
V	na	213	195	208	167
Co	na	280	105	181	14

Figure 5.9. Copper concentrations (ppm) in sediment at Tilt Cove. Darkest areas represent soft sediment. Light areas represent hard bottom. Yellow lines are concentration isograms. Bold Arabic numerals identify biota sampling sites. Additional biota sampling sites are outside the map area.

At Little Bay on-land and marine tailings have similar contents of each of Cu, Ni, V, Mn and Co. These values are high compared to unpolluted estuarine sediments including that from the control site (Table 5.6). As well, most metals

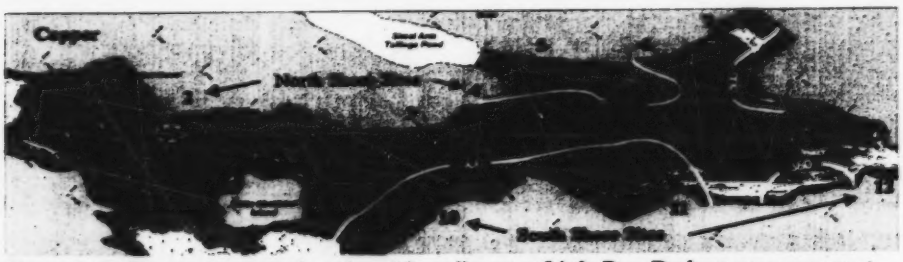

Figure 5.10. Copper concentrations (ppm) in sediment at Little Bay. Darkest areas represent soft sediment. Light areas represent hard bottom. Yellow lines are concentration isograms. Bold Arabic numerals identify biota sampling sites. Additional biota sampling sites are outside the map area.

are remarkably homogeneous within the marine tailings depositional apron in Little Bay Arm (Fig 5.10). There is little evidence for systematic geographic variations in the contents of most metals. The total variation in Cu is <25% (excepting one site) (Near biota site 2 in Fig. 5.10.), compared to a factor of 2.5 in the on-land tailings pile; for Zn <25% (except for one site), compared to a factor

of 1.5 variation on-land. This suggests that the tailings were well mixed during or after marine deposition. As Little Bay is a sheltered estuarine environment, efficient mixing during marine deposition is more probable.

However, concentrations of Pb, Sn and Sb do not exhibit the aforementioned pattern of geographic homogeneity in Little Bay Arm, increasing in abundance toward the opposing shore from Shoal Arm to values much greater than those found in the on-land tailings pile. An exotic (non-tailings) source of Pb, Sn and Sb in Little Bay Arm is indicated. Lead isotopic compositions (Fig. 5.11) suggest contamination by a radiogenic source.

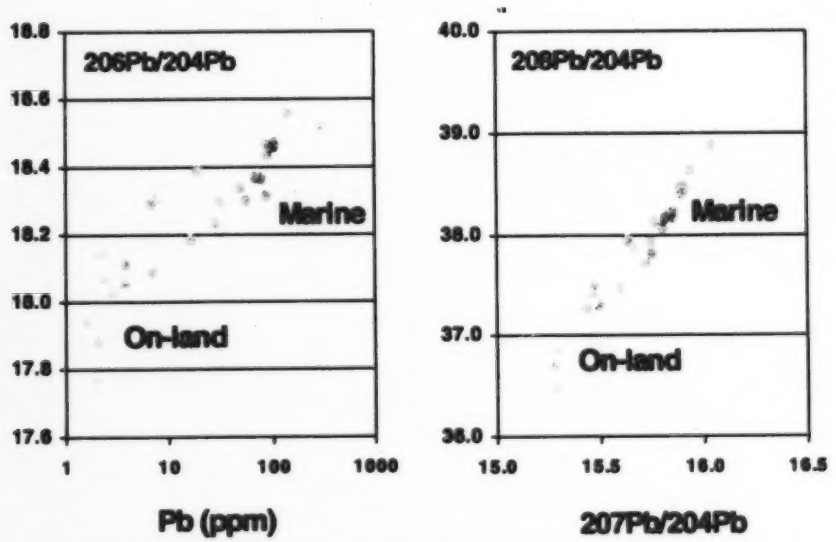

Figure 5.11 Lead isotopic composition of on-land (triangles) and marine (circles) tailings.

5.2.3 Metal concentrations in the near-shore biota

The Veinott et al. (2001) study reported that concentrations of Cu, V, Mn, Co, and Fe were significantly higher in the soft tissue of *Mytilus edulis and Mya arenaria* living in and around the tailings delta at Little Bay compared to a control site. Significant species effects were also reported (their Fig. 1) with *M. edulis* generally having higher concentrations of all metals.

The results from the PCA analysis suggest that the mussels are separated into three clusters (Groups 1, 2, and 3 - Fig. 5.12): Group 1: the two sites in Little Bay adjacent to the dam breach (Biota sampling sites 4 and 5 in Fig. 5.10); Group 2: the Tilt Cove site closest to the tailings outfall pipe (Biota sampling site 4 in Fig. 5.9) and the Little Bay site at the mussel farm loading dock; and Group 3: all other sites. Within group 3, Little Bay sites (triangles) and Tilt Cove sites (circles) are separated. As well, the Little Bay sites further separate into sites within Little

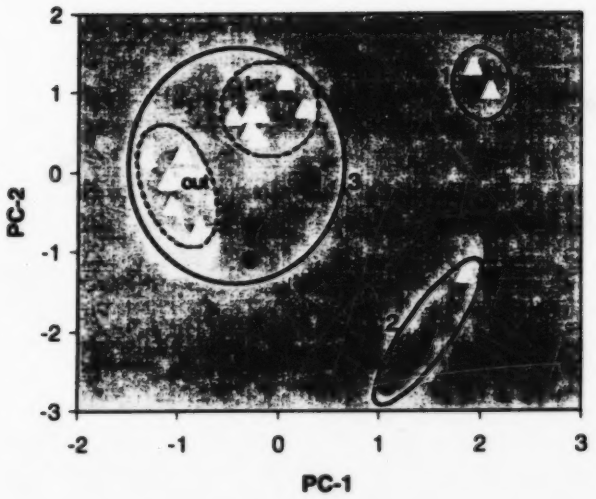

Figure 5.12. Metals in mussels. Plot of scores on the first two principle components. Triangles are Little Bay sites, circles are Tilt Cove sites and the square represents the control site. "out" = outside Little Bay Arm. "in" = inside Little Bay Arm.

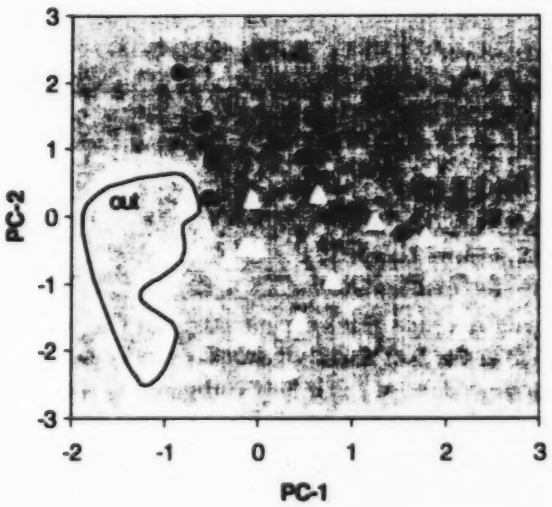

Figure 5.13 Metals in *Fucus* spp. Plot of scores on the first two principle components. Triangles are Little Bay sites, circles are Tilt Cove sites and the square represents the control site. "out" = outside Little Bay Arm.

Bay arm itself (in) and sites outside Little Bay Arm (out). This suggests that the tailings are confined to Little Bay Arm and that PC-1 is a measure of distance from the dam breach. The unusual Little Bay sample in group 2 was collected near the mussel farm loading dock and the individuals from this site may have been escapees from the mussel farm. The lack of mussel sampling sites at Tilt Cove make it difficult to determine if a similar effect is found at Tilt Cove. Nevertheless, the sample collected at the tailings outfall site has elevated concentrations of Pb, Zn, Ba, and Cd, relative to the other samples.

A similar analysis of the *Fucus* spp. in the area resulted in similar trends (Fig. 5.13). Little Bay samples with high negative PC-1 values are outside Little Bay Arm, whereas sites with high positive PC-1 values are those closest to the dam breach. The site with the highest PC-1 value was collected near an old slag heap to the north east of the dam breach (Biota sample site 6 in Fig. 5.10).

The PC-1 separation of the Tilt Cove samples appears to

be based on geographic location. Sites with positive PC-1 values are from Tilt Cove itself and a site to the southwest of Tilt Cove. This is the suspected direction of the movement of the tailings as indicated by the hydroacoustic survey and sediment analyses (Fig. 5.9). Sites with negative PC-1 values are east of the tailings with one western site in a well protected cove.

Combining the mussel and *Fucus* data sets and re-running the principal component analyses produced a separation between species on the first principal component as well as the distance and direction effects noted in the earlier analyses on the PC-2 axis (Fig. 5.14). An examination of the metal loading values revealed that the mussels were elevated in Pb, Cr, Zn, Cd, and V, whereas *Fucus* was elevated in Mn, Ni, As, and Ba. This may be indicative of the route of uptake for the different metals. Mussels are likely sequestering metals from particles and food while *Fucus* are taking up metals from the dissolved phase.

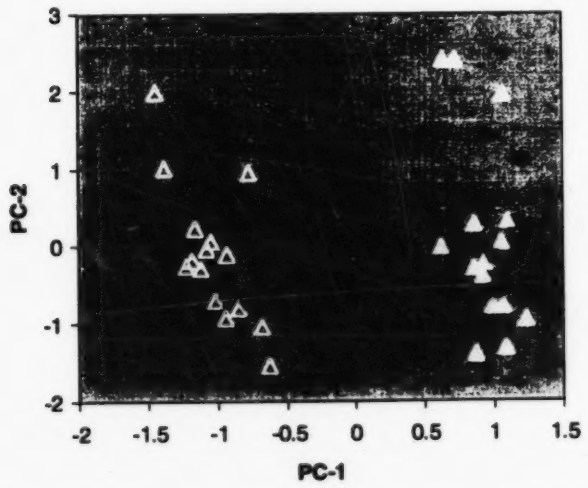

Figure 5.14 Metals in *Fucus* spp and mussels. Plot of scores on the first two principle components. Open symbols represent *Fucus*, closed symbols represent mussels. Triangles are Little Bay sites, circles are Tilt Cove sites and the squares represent the control site.

Copper and cobalt are driving the separation along the PC-2 axis. Samples from sites with high positive PC-2 values are enriched in Cu and Co relative to the other sites.

5.3 ECOTOXICOLOGY

5.3.1 Acute toxicity

There was no evidence of acute toxicity. Tests conducted on juvenile flounder, trout larvae, capelin larvae, and mixed plankton samples produced no difference in survival rates between control organisms and those exposed to tailings.

5.3.2 Bivalve histopathology

An examination of the gill and hepatopancreas tissue of clams living in the tailings delta revealed no evidence of disease. There was also no evidence of clam haemic neoplasia, a disease common in polluted areas. A comparison between the

condition index of mussels from Little Bay and the control site found higher condition indices for the Little Bay mussels.

5.3.3 Bivalve immune response

Tests designed to measure immune response showed that the immune system of the mussels responded in two ways when exposed to Little Bay tailings. First, there was a significant increase in the percent of phagocytized particles in mussels exposed to 200g/L of dry tailings for 2 hours ($p<0.05$). Second, exposure of mussels to tailings leachate caused a significant increase in protein serum levels (Table 5.7). Both these tests suggest that the immune system of the animals

Table 5.7 Serum protein concentrations in mussels exposed to tailings leachate.

Amount of tailings used and grain size (G).	Exposure time and water changes	Serum protein levels (mg/ml)
9 g/L 250μm < G < 500μm	7 days with solution replaced every 2 days	C: 0.62 ± 0.11 E: 0.72 ± 0.29 p = 0.463
12.5 g/L 90μm < G < 250μm	7 days with solution replaced every 2 days	C: 0.62 ± 0.11 E: 0.90 ± 0.22 p = 0.017
19 g/L 75μm < G < 90μm	7 days with solution replaced every 2 days	C: 0.62 ± 0.11 E: 0.95 ± 0.32 p = 0.093
200 g/L Dry whole tailings	7 days with solution replaced every 2 days	C: 0.76 ± 0.18 E: 1.03 ± 0.33 p = 0.113

C = Control, E= Exposure, p = probability of a significant difference

was activated in response to exposure to the tailings. These are detoxifying reactions and suggests that the tailings are perceived as a threat to the health of the animal. However, it is not clear if the response is caused by the presence of toxic metals or if it is a grain size effect.

5.3.4 Oxidative damage

The oxidation of metals such as CuII to CuIII can result in the production of free radicals. Free radicals are extremely reactive and can disrupt cellular function and cause damage to proteins, change membrane structure and function, and damage DNA. There was no evidence of DNA damage in the test organisms. However, there was evidence of oxidative damage to cells and tissue.

The TBA test is a means of detecting oxidative damage in tissues and cells. In laboratory exposures, hepatopancreas tissue in clams exposed to tailings leachate produced significantly more TBA reactive species (TBARS) than the control (Fig. 5.15). This suggests that there was oxidative damage to the tissue. Gill tissue was not affected in the same manner . However, in 1999, clams living at the Little Bay site had significantly higher concentrations of TBARS in their hepatopancreas and their gill tissue compared to the mussels at the control site

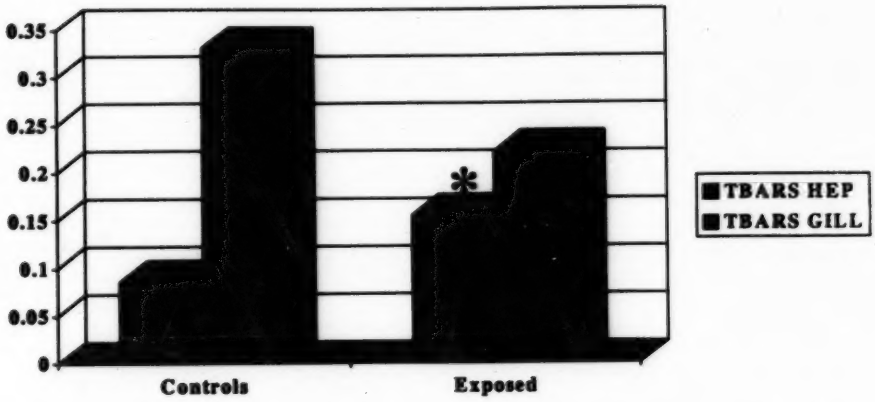

Figure 5.15. TBARS levels (nmol/mg) in clams exposed to tailings leachate (200g/l, 7 days, water renewed 4 times). * indicates a significant difference ($p<0.05$) between exposure and control.

(Fig. 5.16). In the 2000 samples there was no difference in TBARS concentrations between the study animals and the control.

5.3.5 Short term toxicity

Several short term toxicity tests were conducted to examine the effects on benthic organisms. There were no positive results (indicating toxicity) in the Microtox tests. There was a small but significant ($p<0.05$) drop in the survival rate of amphipods exposed to tailings. However, it was difficult to separate grain

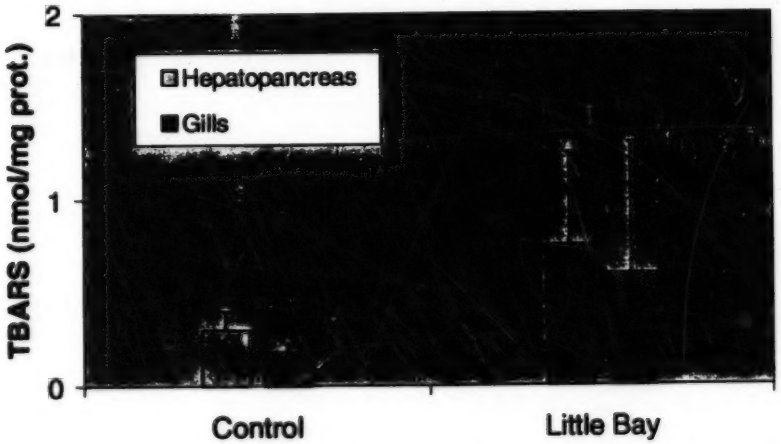

Figure 5.16. TBARS concentrations in clams sampled at Little Bay and the control site.

size effects alone from toxic metal effects. As well, there was a small but significant ($p<0.05$) effect on the growth of polychaetes exposed to 100% tailings (Table 5.8).

Table 5.8. Polychaete growth rates (mg/worm/day)

15% Tailings		100% Tailings	
Little Bay	Control	Little Bay	Control
1.09	1.18	0.83	1.18

5.3.6 Neuroendocrine effects

Trout exposed to tailings lechate became darker (Fig. 5.17). The mechanism for this response is believed to be linked to the endocrine system. The functioning of the cells that control skin pigmentation is believed to be disrupted by the metals in the leachate.

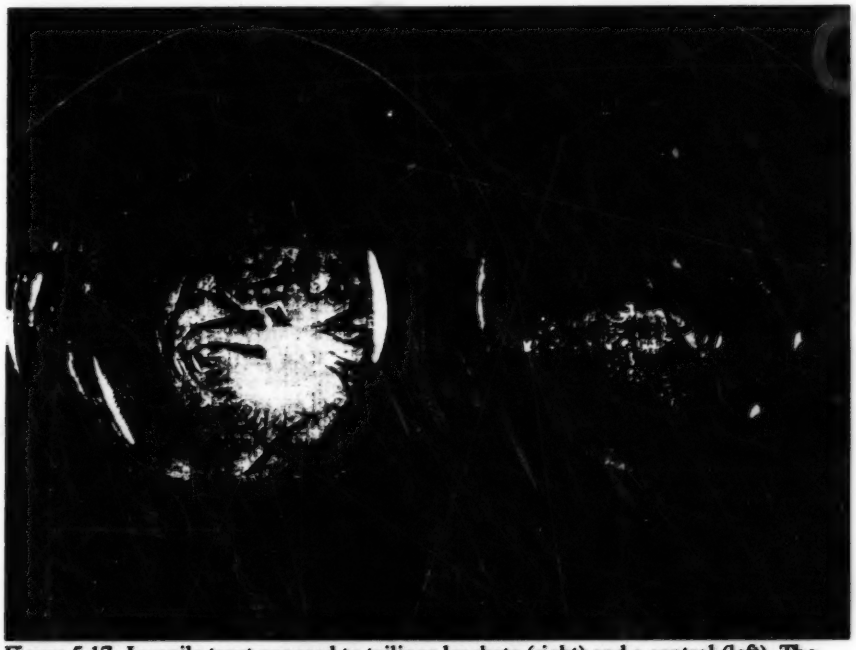

Figure 5.17. Juvenile trout exposed to tailings leachate (right) and a control (left). The fish on the right are darker than the fish on the left

5.3.7 Habitat avoidance

There was no evidence of avoidance of the tailings by juvenile winter flounder. The porportion of time spent on tailings was not statistically different ($p>0.05$) than the time spent on the control sediment (Fig 5.18).

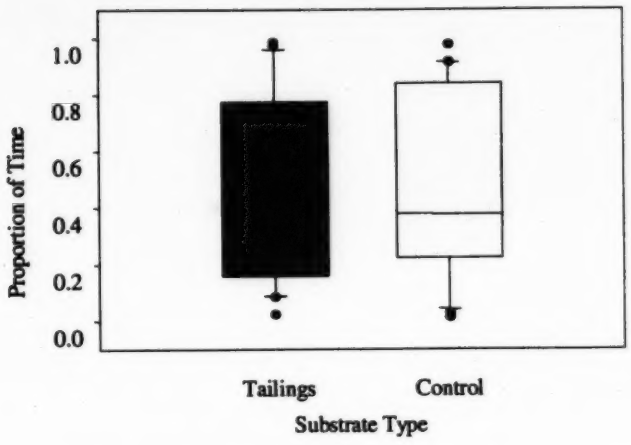

Figure 5.18. Proportion of time juvenile winter flounder spent on either tailings or control sediment.

5.3.8 Benthic community structure

The tailings delta at Little Bay was not devoid of life. Table 5.9 lists the abundance and number of species recorded in 3 sediment samples.

Table 5.9. Analysis of the benthic community at Little Bay.

	Sample		
	1	2	3
Abundance	44	33	47
Number of Species	8	8	15

6 DISCUSSION

STD is sometimes an attractive option for coastal mine operators. Proponents of the STD option argue that it has all the advantages of subaqueous terrestrial disposal (reduced oxidation, reduced acid generation, reduced metal release) without the need or risk associated with dammed enclosures (dam failure, flooding, spills, etc). However, as Poling and Ellis (1995) pointed out, detailed mineralogical, leaching, and oceanographic studies are necessary at every site where STD is being considered.

6.1 CHEMICAL ASSESSMENT

Despite their close geographic proximity and similar ore bodies, the tailings from the two sites in this study were quite different in their chemical composition and behaviour. Although neither site's tailings were inert, Little Bay tailings were, overall, less reactive. In the 18-hour leach test, which simulates the reaction of the tailings to exposure to a different environment, the Little Bay tailings released less Pb, Ni, and Zn, than the Tilt Cove tailings. This was the case for both fresh and saline waters. However, the saline leach resulted in the release of significantly higher concentrations of Pb than did the fresh water leach (Table 5.1). The mechanism for this is possibly the formation of lead chloride complexes as demonstrated in the galvanic interaction study. This raises the question whether metal contamination around the Black Angel Mine in Greenland (Asmund 1992) is due to dissolution of secondary alteration products or in-situ leaching of primary sulphides through galvanic interaction.

As well, the Little Bay tailings were less reactive during the lysimeter tests. There was no acid generation under either the fresh or saline water cover conditions, therefore, no release of metals (Fig. 5.3, 5.4). The Tilt Cove results showed significant oxidation, acid generation, and release of contaminants to the surface water column from the underwater deposited tailings (Fig. 5.5, 5.6). However, the results were somewhat complicated by the presence and dissolution of the previously accumulated oxidation reaction products, which impacted both the surface and porewater regimes. In this scenario, it was difficult to separate the independent contribution of the surface reactivity of the underwater deposited Tilt Cove tailings from that related to their previous oxidation history.

Without further tests on unoxidized Tilt Cove tailings it is not possible to ascertain the extent of oxidation and release of metals from these tailings if they were deposited in a marine environment. Furthermore, the lysimeter tests were conducted under shallow water cover and no flow conditions, which were conducive to enhanced surface reactivity under laboratory controlled conditions. Therefore, any release of metals in a true disposal operation would be expected to be different and possibly of lower concentrations and at a slower rate than was observed in the present study.

6.2 METAL DISTRIBUTION IN BIOTA AND SEDIMENT

Veinott et al. (2001) reported that concentrations of Cu, V, Mn, Co and Fe were significantly higher in the soft tissue of mussels and clams living in and around the Little Bay tailings compared with a control site. Our research confirms this and further suggests that the total metal burden for mussels in Little Bay is dependent on their proximity to the tailings dam breach (Fig. 5.12). Similar findings were reported by the Larsen et al. (2001) study which reported a distance effect on the concentration of Pb and Zn in mussels and seaweed after a mine closure.

The separation of mussels and seaweed in the PCA (Fig. 5.14) suggests different uptake routes by the different organisms. Seaweeds are generally seen as good indicators of available dissolved metals, whereas mussels uptake metals from the dissolved phase, in their food, and from non-food particles (Rainbow 1995). The results of the PCA therefore, predict that Ba, As, Mn, and Ni are in the dissolved phase while Pb, Zn, Cd, Cr, and V are bound to particles. Further work would be required to confirm this.

The separation of Little Bay sampling sites along PC-2 (distance from the tailings dam breach) in figure 5.14 is driven primarily by Cu and Co concentrations. Yet, the distribution of Cu in the sediments in Little Bay Arm is nearly uniform. The expectation would be for Cu to be evenly distributed within the biota. However, the biota samples near the dam breach contain much higher concentrations of copper. Either the copper is more available or exposure times to dissolved or particulate Cu is greater. The sequential extraction data (Fig. 5.2) indicates that as the marine environment is approached, carbonates rather than sulphides become an important fraction in which Cu is bound. The copper in the carbonate fraction would be more bioavailable and may explain the distribution within the biota. Unfortunately time and resources did not permit the carrying out of sequential extractions on all the sediment samples collected, so it is not known if the partitioning of the metals changed with distance from the dam breach.

In contrast to the homogeneous distribution of Cu in the sediment (Fig. 5.10), Pb in Little Bay is unevenly distributed. The increased concentration along the shore opposite the tailing pond is believed to be from an exotic source of Pb (Fig. 5.11). One possibility is contamination from paint from the hulls of ships. However, the Pb anomaly does not appear in the biota. This is especially surprising for *Mytilus* spp. because of their propensity for accumulating trace metals (Boening 1999; Rainbow and Philips 1993), and suggests that the Pb is in a non-available form. Unlike Cu, which partitioned into the carbonate fraction, the concentration of Pb in the exchangeable and carbonate fractions of the sediment was insignificant.

At Tilt Cove, the partitioning of the metals in the marine sediment were similar to Little Bay sediments. Minor differences in metal partition patterns at the two sites are likely related to their orders-of-magnitude differences in various metal contents. As well, absolute concentrations of metals in the biota were similar between the two sites despite the differences in the potential metal loads at the two sites (Table 5.6). However, the distribution pattern of metals in the

sediments suggests that the tailings are migrating on a westerly trend away from Tilt Cove. High copper concentrations (2000 ppm) were measured in a sediment sample collected from the western edge of the hydroacoustic survey area (Fig. 5.9). The hydroacoustic survey area was also the defined sediment survey area so no samples were collected outside these boundaries. However, the PCA of the seaweed data revealed a separation of Tilt Cove sites into eastern and western collection areas (Fig. 5.13). Sites around Tilt Cove and west had higher concentrations of copper and cobalt compared to the sites east of Tilt Cove. The exception was a site just west of Tilt Cove that was behind a promontory known as Scrape Point. It is possible that Scrape Point diverts any tailings away from the near shore in this area.

6.3 ECOTOXICOLOGY

The presence of metals in an ecosystem does not necessarily constitute an environmental or health risk. Even elevated levels of metals in biota does not prove that the organisms are suffering from any adverse effects. As was noted in the Veinott et al. (2001) study, bivalves from Little Bay, although they had elevated concentrations of metals in their soft tissue, the concentrations did not exceed the USFDA "levels of concern" for those specific metals in shellfish. Furthermore, it is generally recognized that tailings are not acutely toxic as was the case in this study. There was no evidence of acute toxicity to juvenile flounder, trout or capelin larvae, or mixed plankton samples. As well, there were no obvious signs of disease in mussels or clams at Little Bay. Therefore, the focus of the ecotoxicology discussion will be on chronic effects of exposure to these tailings.

Many studies report effects from exposure to mine tailings, and the effects range in scale from the community to the cellular level. For example, Farina and Castilla (2001) reported a drastic reduction on the sessile species diversity in intertidal rocky shores affected by copper mine tailings. The Payne et al. (2001) study reported a marked reduction in skin pigmentation of trout in a lake contaminated by iron-ore. In our study, several tests produced responses that suggest there are effects on the biota from chronic exposure to the tailings.

One mechanism of potential toxicity is oxidative damage, details of which are given in Hamoutene et al. (2001). Briefly, oxidation of Cu through the Fenton Reaction can result in the production of free radicals. These free radicals are highly reactive ions that can damage lipids, proteins, and DNA. Oxidative stress induced by exposure to pollutants can compromise the health of aquatic organisms (see DiGiulio et al.1989 for a review). In the first sampling year of the study, lipid peroxidation (TBARS) levels were elevated in tissues (gills and hepatopancreas) of clams collected from Little Bay relative to the control site (Fig. 5.16), and in laboratory studies of clams exposed to tailings lechates (Fig. 5.15), suggesting oxidative damage had occurred. In the second sampling year there was no difference in TBARS levels in clam tissues taken from the study site and the control site. However, catalase activities in the clams was increased in the second year and may have acted as an antioxidant. The clams, therefore, may be

able to protect themselves from lipid peroxidation induced by exposure to the tailings. However, catalase activity can fluctuate seasonally (Cossu et al. 1997) and the differences in TBARS may be related to a difference (October and November) in sample collection dates between the two years.

The involvement of metals like iron or copper in the increased reactive oxygen species production is intimately related to the level of DNA oxidative damage (Meneghini 1997). Therefore, the Comet assay was used to determine DNA damage levels in clams during the second year of sampling. No differences in DNA damage were found between samples from the mining and control sites. It may be that euryoxic organisms such as intertidal bivalves have very effective antioxidant defenses to combat major increases in oxyradical production (Livingstone et al. 1990) and thus no consequences can be observed on DNA damage levels.

Phagocytosis (the engulfing of particles) is a detoxifying mechanism employed by many organisms. Any increase in the number of particles engulfed by cells upon exposure to a potentially toxic substance is generally interpreted as an enhancement of the detoxifying response. The immune system is activated and the substance in question is precieved as a threat to the health of the organism. A similar interpretation is given to any increase in serum protein levels upon exposure to a potential toxin.

Both of the above mentioned responses were observed during tests conducted on mussels from Little Bay exposed to tailings leachate. The number of phagocytized particles increased and serum protein levels increased (Table 5.7). Although, the increase in the number of phagocytized particles was not significantly greater ($p=0.052$) than the control, combined with the evidence of oxidation damage, a significant increases in serum protein levels, a decrease in the survival rate of amphipods, an effet on growth rates of polychaetes (Table 5.8) and the observed neuroendocrine effect on trout (Fig. 5.17), the weight of evidence suggests that the tailings are stressing the animals.

Nevertheless, the tailings at Little Bay are sustaining a large population of clams and the sediment is not devoid of life (Table 5.9). Re-colonization of tailings is common (Kline and Stekoll 2001; Burd et al. 2000; Ellis and Hoover 1990) and the soft shell clam (*Mya arenaria*) likely is an opportunistic invader of the Little Bay tailings delta. *M. arenaria* was the only macroscopic organism observed in clay-like tailings at an abandoned mine in British Columbia (Levings 1975) and suggests that they may have a tolerance for metal-enriched environments. As well, *Mytilus* spp. are notorious for surviving in heavily contaminated areas which is why they are used a biomonitors world wide. No tests were conducted to compare species diversity with non-polluted sites, but the organisms at the study sites seem very capable of tolerating the metals in their environment.

7 CONCLUSIONS

The primary objective of this project was to assess the long-term environmental and ecotoxicological consequences of submarine tailings disposal.

We have met this objective by carrying out a detailed evaluation of the chemical properties of the tailings, determining the movement and fate of metals released from the tailings, and assessing the toxicological consequences for marine fish and shellfish. Integration of the physical, chemical, biological, and ecotoxicological characteristics of the two sites permitted a realistic determination of the risks associated with marine tailings disposal.

Although there were no obvious indications of large scale environmental damage to the marine environment at either site, we conclude that neither site would be considered suitable for a submarine tailings disposal operation. At Little Bay, the benthic community was certainly destroyed at the time of the dam failure. Further, the topography of Little Bay Arm has confined the tailings to a relatively small geographic area. The method of disposal (dam failure) almost certainly is the cause for the increased metal loads in the biota near the dam breach. However, the unique metal signature of the biota within Little Bay Arm suggests that tailings are impacting the entire near shore zone. As well, we provided evidence of an immune system response by the biota in the area, which suggests that the tailings are perceived as a threat to the health of the animals

At Tilt Cove, disposal of the tailings through an outfall pipe directly into 50m of water did not prevent the near shore biota from accumulating trace metals abundant in the tailings. Further, the tailings appear to have moved out of the study area, so the geographic range of the impact zone is not accurately known. Therefore, neither Tilt Cove nor Little Bay are suitable locations for submarine tailings. Based on the weight of evidence, near shore disposal of mine wastes in areas with similar topographic and oceanographic characteristics as Tilt Cove or Little Bay are not recommended. However, we acknowledge that current best practices in the mining industry would not currently sanction the use of either of these sites.

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